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AFRPL-TR-69-31

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(TITLE UNCLASSIFIED)

INVESTIGATION OF THE THERMODYNAMIC
PROPERTIES OF PROPELLANT INGREDIENTS

ANNUAL PROGRESS REPORT AFRPL-TR-69-31

(1 January 1968 to 31 December 1968)

January 1969

AIR FORCE ROCKET PROPULSION LABORATORY

RESEARCH AND TECHNOLOGY DIVISION

EDWARDS AIR FORCE BASE, CALIFORNIA

1969

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This document consists
of 63 pages, copy
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Report Nr. T0025-4Q-68

ANNUAL PROGRESS REPORT (U)

(1 January 1968 to 31 December 1968)

January 1969

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA 93523
CONTRACT NR. F04611-67-C-0025

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CHEMICALS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. F04611-67-C-0025. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148. "Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This annual report covers the work performed during 1 January 1968 through 31 December 1968. The Dow Report Number is T0025-4Q-68.

This work was performed by G. C. Sinke, A. C. Swanson, and L. C. Walker, under the technical supervision of Dr. D. R. Stull and management supervision of Dr. D. A. Rausch.

This report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

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ABSTRACT

(C) The heat of formation of crystalline perfluoroammonium fluoborate (NF_4BF_4) was derived from measurements of the heat of decomposition to NF_3, BF_3, and F_2 as -337.4 ± 2.5 kcal/mole. Infrared spectra and mass spectra verified the expected decomposition products and also indicated the sample to be of good purity.

(U) The binder ingredients PBAA and PBAN were analyzed as $C_{7.11006}H_{10.91302}O_{0.41376}S_{0.03119}N_{0.02142}$ and $C_{6.89359}H_{10.21855}O_{0.13751}N_{0.22846}S_{0.03119}Cl_{0.01410}$, respectively. The heats of formation, determined by standard oxygen bomb calorimetry, were -8.28 kcal/100 g PBAA and -0.70 kcal/100 g PBAN.

(C) Heats of combustion of aminoethylaziridine, $C_4H_{10}N_2$ (Code ELF-100), and methyldiazabicyclooctane, $C_7H_{14}N_2$ (Code ELF-101), were measured by standard oxygen bomb calorimetry. Derived heats of formation of these liquids were $+12.68$ kcal/mole for ELF-100 and $+2.99$ kcal/mole for ELF-101.

(C) A sample of methylene bisoxyamine, $CH_6O_2N_2$, was submitted by AFRPL, Edwards Air Force Base, for oxygen bomb calorimetry. The heat of formation derived from the combustion calorimetry studies was -24.12 kcal/mole for the liquid sample as received.

(U) The heat of formation of CF_3NF_2 gas was derived from its heat of reaction with NF_3. The reaction was triggered by addition of cyanogen. The result, -168.9 kcal/mole, is in good agreement with bond energy predictions and with a linear relation for the heats of formation of the series $CF_x(NF_2)_{4-x}$.

(U) Measurements of the heats of mixing of aqueous hydrazine and aqueous HCl led to an improved value for the heat of formation of ClF_5 (g) as -62.4 kcal/mole (based on -77.01 kcal/mole for HF, 22.8 H_2O).

(U) Techniques for the heat of combustion of organic chlorine compounds were checked by measurements of the heat of combustion of aniline hydrochloride crystal. The value found agreed well with an independent result based on solution calorimetry. This indicates that our chlorine compound combustion techniques are reliable and can be used on such compounds as organic perchlorates.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Contd.)

SECTION I

(U) THERMOCHEMISTRY

A. THE HEAT OF FORMATION OF PERFLUOROAMMONIUM FLUOBORATE (C)

1. Introduction (U)

(C) Perfluoroammonium fluoborate (NF_4BF_4) was first synthesized at Shell Development Company. A 5 gram sample was supplied to us for thermochemical studies. The preparation of this relatively large amount required a strenuous endeavor by Shell personnel and therefore optimum use of the sample was a fac'or in our studies.

(C) The NF_4BF_4 was a white, free flowing, crystalline material. Analytical data supplied by Shell Development Company showed the sample to be of high purity. Due to the limited amount of sample, no preliminary analyses were carried out at Dow. Apparatus for heat of decomposition studies to be described was designed to allow collection and identification of the decomposition products; these experiments confirmed the sample to be of good purity.

2. Heat of Combustion Approach (U)

a. Method (U)

(C) The first attempts to determine the heat of formation of NF_4BF_4 were based on the technique for boron compounds described by Good and Mansson (1). In this technique the boron-containing compound is intimately mixed with powdered polyvinylidene fluoride (trade name Kynar) in a plastic film bag. The bag is rolled tightly and compressed into a solid pellet. When burned in oxygen in a rotating combustion bomb containing water, the boron volatilizes as BF_3 and dissolves to form aqueous HBF_4. Although this approach proved unsuccessful, the results will be briefly described.

b. Materials (U)

(U) A sample of polypropylene film, heat-set, balanced biaxially oriented, 50 mil gauge, type B500, was obtained from Hercules Incorporated, Cleveland, Ohio. Two samples of the polypropylene film were analyzed for carbon and hydrogen. The average carbon was 85.1%. The average hydrogen was 14.3%. When these percentages were normalized they became 85.6% carbon and 14.4% hydrogen, which agrees exactly with a theoretical molecular weight of 42.08112 for C_3H_6.

(U) A sample of Kynar was supplied by the Pennsalt Chemicals Corporation. A portion of the Kynar used by Good and Mansson (1) was supplied through the courtesy of Dr. W. D. Good of the

Thermodynamics Laboratory at the Bureau of Mines in Bartlesville, Oklahoma. Analyses by Dr. Good indicated his sample agreed within experimental error with the composition $(C_2H_2F_2)n$.

(U) In combustions involving the Pennsalt sample, mass spectroscopic analysis of the bomb gases after combustion showed no trace of CF_4. The Pennsalt sample was powdered but no screened; the Good sample was screened to 100 mesh particle size and finer.

c. Equipment (U)

(U) A typical rotating bomb calorimeter and a platinum-lined combustion bomb were employed.

d. Procedure (U)

(U) The polypropylene film was pelleted and burned in the usual fashion in a covered platinum crucible. The Kynar samples were pelleted after being sealed in polypropylene film bags as described by Good and coworkers (1,2).

(U) A weighed polypropylene bag containing a weighed amount of Kynar was locked into a dry box. Approximately the desired amount of NF_4BF_4 was weighed out on a small balance in the dry box and added to the polypropylene bag. The bag was heat sealed while in the dry box and the Kynar and NF_4BF_4 intimately mixed by manipulation of the sealed bag. A pinhole was pricked in the bag to allow trapped gas to escape and the bag was rolled up and compressed in a press to form a pellet. The pellet was placed in a second weighed polypropylene bag which was then heat sealed, removed from the dry atmosphere, and accurately weighed. The sample thus enclosed did not pick up weight when weighed in the laboratory air.

(U) The weighed sample was placed in a platinum crucible in a platinum-lined bomb. The bomb also contained 10 ml of water, and after sealing was charged with purified oxygen to 40 atm pressure. The heat of combustion was determined by the usual techniques. A sample of the gaseous combustion products was analyzed by mass spectrometry. The calorimeter has been calibrated with N. B. S. benzoic acid in eighteen experiments to date. The $E(calor) = 3515.71 \pm 0.23$ cal/deg.

e. Calorimetric Results (U)

(U) The calorimeter data for the diluent, Kynar, and the polypropylene film bags were processed by a computer program. Constant factors used as input for the program are given in Table I and other variables in Tables II, III and IV.

Table I

(U) Constant Factors in Combustion Calculations of Vinylidene
Fluoride Polymer (Kynar) Pelleted in Polypropylene Bags

Empirical formula of Kynar	$C_2H_2F_2$
Empirical formula of polypropylene film	C_3H_6
Empirical formula of fuse	$C_1H_{1.8}O_{0.9}$
Density of Kynar	1.775
Density of film	0.905
Density of fuse	1.5
Bomb volume, liter	0.347
Initial oxygen pressure, atm	40
Initial water in bomb, g	20.0
Reference temperature, °C	25
Final ratio, H_2O/HF	10
$(\delta E/\delta P)_T$ of Kynar, cal/g/atm	-0.00189
$(\delta E/\delta P)_T$ of film, cal/g/atm	-0.00310
$(\delta E/\delta P)_T$ of fuse	Negligible
ΔE_c^o of polypropylene film, kcal/mol	-466.08
ΔE_c^o of fuse, kcal/mol	-111.7
Cp of Kynar, cal/g/°C	0.33
Cp of polypropylene film, cal/g/°C	0.315
Cp of fuse, cal/g/°C	0.4
E(Calor), cal/°C	3414.71

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Table II

Heat of Combustion Experiments for Polypropylene Film (U)

Parameter	Experiment Number					
	1	2	3	4	5	6
Polypropylene film, g	0.495322	0.706585	0.694298	0.692345	0.687392	0.78649
Fuse, g	0.003245	0.003025	0.002265	0.002746	0.003692	0.002374
Mass of added Pt, g	51.3568	51.3568	51.3568	26.2020	51.3226	51.3226
t_i, °C	23.411734	22.741424	22.72907	22.716639	22.729064	22.413980
t_f, °C	25.082979	25.100469	25.050131	25.032784	25.033044	25.039224
Δt corr., °C	0.059948	0.063375	0.066115	0.067707	0.070110	0.072363
$-\Delta Ec/M$, cal/g	11082.00	11077.20	11077.24	11070.96	11075.60	11071.65

Parameter	7	8	9	10	11	12
Polypropylene film, g	0.681330	0.642903	0.661022	0.667007	0.620310	0.614823
Fuse, g	0.002881	0.003960	0.002422	0.002370	0.002790	0.002663
Mass of added Pt, g	45.3100	45.3100	51.2461	56.3494	51.0084	51.0084
t_i, °C	22.966793	22.903863	22.816202	22.797502	22.947876	22.973144
t_f, °C	25.227372	25.053839	25.033161	25.024449	25.036675	25.038048
Δt corr., °C	0.055166	0.067653	0.0719199	0.061384	0.073085	0.067742
$-\Delta Ec/M$, cal/g	11077.10	11076.24	11066.52	11073.54	11078.14	11074.79

Average $-\Delta Ec/M$ = 11075.1
Std. Dev. = ±1.0 cal/g

Table III

Heat of Combustion Experiments for Kynar Sample No. 1 (Pennsalt) (U)

Parameter	Experiment Number					
	1	2	3	4	5	6
Kynar, g	2.039493	0.099811	2.139699	1.986037	2.033933	2.118192
Film, g	0.067961	0.070654	0.066462	0.066971	0.069368	0.069840
Fuse, g	0.003456	0.003500	0.002878	0.003071	0.002715	0.002580
Moles HF(x10²) final	6.36699	6.5583	6.6829	6.2030	6.3526	6.6157
Mass, added Pt, g	51.3217	51.3217	51.3217	51.3217	51.3217	51.2461
t_i, °C	22.68545	22.74134	22.66070	22.86008	22.80998	22.53696
t_f, °C	25.08659	25.19776	25.15065	25.18590	25.19269	25.02386
Δt corr., °C	0.07247	0.05777	0.06318	0.05638	0.05634	0.07277
$-\Delta Ec/M$, cal/g	3539.5	3537.8	3539.8	3538.7	3539.0	3538.1

Parameter	Experiment Number				
	7	8	9	10	11
Kynar, g	2.099204	2.096452	2.121390	2.243424	2.185606
Film, g	0.063175	0.070906	0.070531	0.066732	0.067697
Fuse, g	0.003367	0.002432	0.002596	0.002720	0.003367
Moles HF(x10²) final	6.5564	6.5478	6.6252	7.0069	6.8263
Mass, added Pt, g	51.2461	51.2461	51.2461	51.2461	51.2461
t_i, °C	22.58023	22.55539	22.53697	22.41402	22.47539
t_f, °C	25.02586	25.02237	25.02903	25.01854	25.02555
Δt corr., °C	0.07063	0.07210	0.07216	0.07143	0.07319
$-\Delta Ec/M$, cal/g	3539.9	3538.0	3538.5	3537.6	3537.0

Average $-\Delta Ec/M$ = 3538.5 cal/g
Std. Dev. = ±0.28 cal/g

-5-

Table IV

(U) Heat of Combustion of Vinylidene Fluoride Polymer (Kynar) Sample #2

Parameter	Experiment Number		
	1	2	3
Kynar, g	2.145502	1.569064	2.102306
Film, g	0.068287	0.071116	0.067739
Fuse, g	0.003300	0.003007	0.002200
Moles HF($\times 10^2$) final	6.7010	5.1228	6.5661
Mass, added Pt, g	51.0084	51.0084	51.0084
t_i, °C	22.51850	23.09928	22.56779
t_i, °C	25.02229	25.01646	25.02236
Δt corr., °C	0.07200	0.06934	0.07004
$-\Delta Ec/M$, cal/g	3527.8	3528.1	3528.3

Average $-\Delta Ec/M$ = 3528.1 cal/g

Max. Dev. = ± 0.5 cal/g

Table V

(C) Heat of Combustion of NF_4BF_4

Expt. No.	Mass Polypropylene, grams	Mass Kynar, grams	Mass NF_4BF_4, grams	$-\Delta Ec/M$, cal/g
1	0.13076	1.38462	0.06738	1003
2	0.13983	1.67173	0.68265	990
3	0.10523	1.36214	0.49074	522
4	0.15707	1.32800	0.48851	743

(U)   There were occasional traces of soot or carbon found in some of the combustions. However, as shown in Table V, there is no apparent trend in $\Delta E_C^\circ/M$ values with or without traces of carbon after combustion. Three combustions on the sample supplied by Dr. Good (Table IV, Sample Nr. 2) gave an average $-\Delta E_C^\circ/M = 3528.1$ cal/g, in excellent agreement with 3527.8 ± 0.6 cal/g determined by Good and Mansson (1). The Pennsalt sample (Table III, Sample Nr. 1) gave an average $-\Delta E_C^\circ/M$ -3538.5 cal/g, indicating slight differences in composition and/or crystallinity. The precision of the measurements is very satisfactory and the accuracy is confirmed by the agreement with Good and Mansson.

(U)   Data for the polypropylene film (Table II) also show excellent precision. These auxiliary data appear to be satisfactory.

(C)   A brief summary of the heat of combustion results on NF_4BF_4 is given in Table V. The experiments by visual observation of the bomb after combustion appeared to be successful in that no unburned residues were observed and mass spectrometry revealed the expected gaseous product CO_2 and traces of CF_4. The calculated heats of combustion, however, showed wide variations. Possible causes for these variations were researched as follows:

(a)   Deterioration of the Sample - A few milligrams of sample were allowed to stand exposed to the dry box atmosphere over the weekend. No changes in the sample appearance were observed, making deterioration an unlikely cause.

(b)   Water Associated with the Kynar - Karl Fischer analyses for water before and after drying the Kynar at 120°C. overnight indicated no appreciable water in the Kynar.

(c)   Incomplete Combustion - Visual inspection of the bomb and mass spectrometer analysis of gaseous products showed no evidence for incomplete reaction.

(d)   Reaction of Kynar and NF_4BF_4 - This appears to be the only plausible cause, but, if it took place to the extent indicated by the heat of combustion data, one would expect considerable and obvious gas formation in the sealed bags. This was not observed.

Because of the limited amount of sample and the considerable expense of its synthesis, it was not practical to investigate variations in the heat of combustion technique. Chances of success were believed too small to risk the use of more sample.

3. Differential Scanning Calorimeter Technique   (U)

(U)   The Thermal Research Laboratory recently acquired a Perkins-Elmer Differential Scanning Calorimeter which is suited for measurement of heat capacity, heats and temperatures of phase transitions, and heat of reaction with moderate accuracy. The

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advantage of the DSC is that results can be obtained on a few
milligrams of sample. The sample is enclosed in a small aluminum
capsule and is then heated so that its temperature rises at the
same rate as that of a reference capsule containing the calori-
metric standard material, Al_2O_3. The rate at which energy is
supplied to the sample is recorded and, for example, if a sample
undergoes melting, a peak is observed in the rate of heating,
since the heat of melting must be supplied in a short time.
From the area under the peak, the heat of melting can be determined.

(C)   Since Shell Development Company personnel reported to
us that NF_4BF_4 decomposes to NF_3, BF_3, and F_2 at relatively low
temperatures, it seemed worthwhile to attempt a measurement of
the heat of decomposition in the DSC. Preliminary measurements
at Shell indicated a heat of decomposition of about 8 cal/g.

(U)   A copy of the recorder output (heating rate) as a func-
tion of temperature is shown in Figure 1. The sample when heated
showed a small increase in heat absorption in the range 500-510°K.
Heating was stopped at about 520°K and the capsule containing
the sample was cooled and weighed. Only 2 to 3% of the sample
weight was lost, and it was concluded that the heat absorption
was a reversible phase transition. This was confirmed when the
sample was heated again to 520°K and the same heat absorption
was observed at 500-510°K. Integration of the area under the
peak gave a heat of transition of 13 cal/g. It seems likely
that it was this heat of transition which was observed by Shell
Development Company personnel.

(C)   Heating was now continued above 520°K, and at about 560°K
it was evident that an endothermic process was taking place. Also
the instrument exhaust port began fuming, indicating the escape
of reactive vapors. This endothermic process appeared to be com-
pleted by 620°K, at which point the capsule was cooled and weighed.
A weight loss corresponding to 99.5% of the sample was observed.
From the area under the peak it was roughly calculated that the
heat of decomposition was 80 cal/g. This is somewhat uncertain
because of difficulty in judging where to draw the baseline. The
corrosive vapors emitted by the sample had seriously affected the
instrument as shown by blank runs following this work. For this
reason, no further runs were made and the single datum obtained
was the basis of a preliminary heat of formation of NF_4BF_4 of
-318.8 ± 10 kcal/mole. From later work to be described, it is
evident that the uncertainty was underestimated.

(U)   This work with the differential scanning calorimeter
was promising enough that an apparatus was developed which was
designed to yield more accurate heats of decomposition as well
as make it possible to collect and identify the decomposition
products.

TEMPERATURE, °K

500 520 540 560 580 600
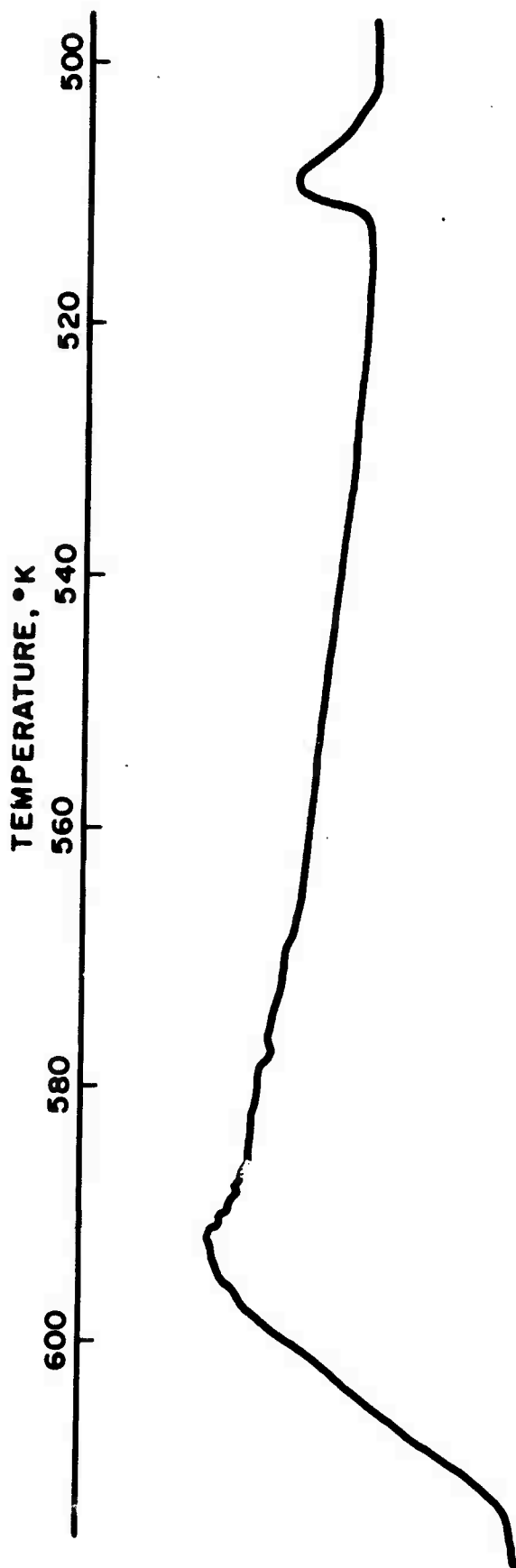
(C) Fig. 1 - Differential Scanning Calorimeter
Trace of Decomposition of NF_4BF_4

4. Heat of Decomposition Studies of NF₄BF₄ (C)

a. Apparatus (U)

(U) The first attempt at a custom apparatus for heat of decomposition was a nickel crucible wound with a glass insulated constantan heater and suspended in a nickel combustion bomb. When the sealed bomb was placed in a combustion calorimeter and the crucible electrically heated, the crucible became hot enough to decompose NF_4BF_4 and the electrical heat was about equal to that of a typical combustion experiment. Blank runs showed excellent precision. However, when a sample of NF_4BF_4 was tried, an exotherm was observed rather than the expected endothermic effect. Mass spectrometer examination of the gases showed the expected NF_3, but also large amounts of SiF_4 rather than BF_3. The reaction of the F_2 and BF_3 with the very dry glass insulation was not expected, since there are literature reports of successful fluorine combustion carried out in glass apparatus.

(C) A second attempt, which proved successful, was designed to eliminate the deficiencies noted above. An all-nickel chamber was fabricated from a discarded combustion bomb head, a short length of nickel pipe and an ordinary commercial crucible. These parts were brazed together with high nickel alloy as shown in Figure 2. A lid for this chamber was fabricated from 1/8" sheet nickel, to which was brazed a stainless steel Hoke valve and a stainless steel tube for lead exits. The chamber and lid were mounted in a combustion bomb as shown in Figure 2. The heater wires are thus isolated from the corrosive gases liberated by decomposition of NF_4BF_4.

(U) The combustion bomb thus modified was placed in an ordinary combustion calorimeter equipped with the usual thermostatted bath and a thermistor as a thermometer.

b. Procedure (U)

(U) The apparatus was thoroughly dried, assembled, connected to a vacuum line and evacuated. The inner chamber was then charged with pure fluorine to a pressure of 500 mm and the heater was subjected to three heating cycles, each similar in intensity and duration to that used for decomposition runs. This "conditioning" procedure formed a protective coating of NiF_2 on the chamber walls and insured complete removal of any residual moisture. The fluorine was then pumped out and the conditioned apparatus was locked into a monitored dry box. Approximately 0.150 g of sample was placed in a polyethylene vial; the vial was removed from the box, weighed, and returned. The apparatus was disassembled, the sample was charged to the inner chamber, and the apparatus was reassembled. The vial was removed from the box and weighed to obtain the exact sample weight by difference. The inner chamber was evacuated and the loaded bomb placed in an isoperibol calorimeter.
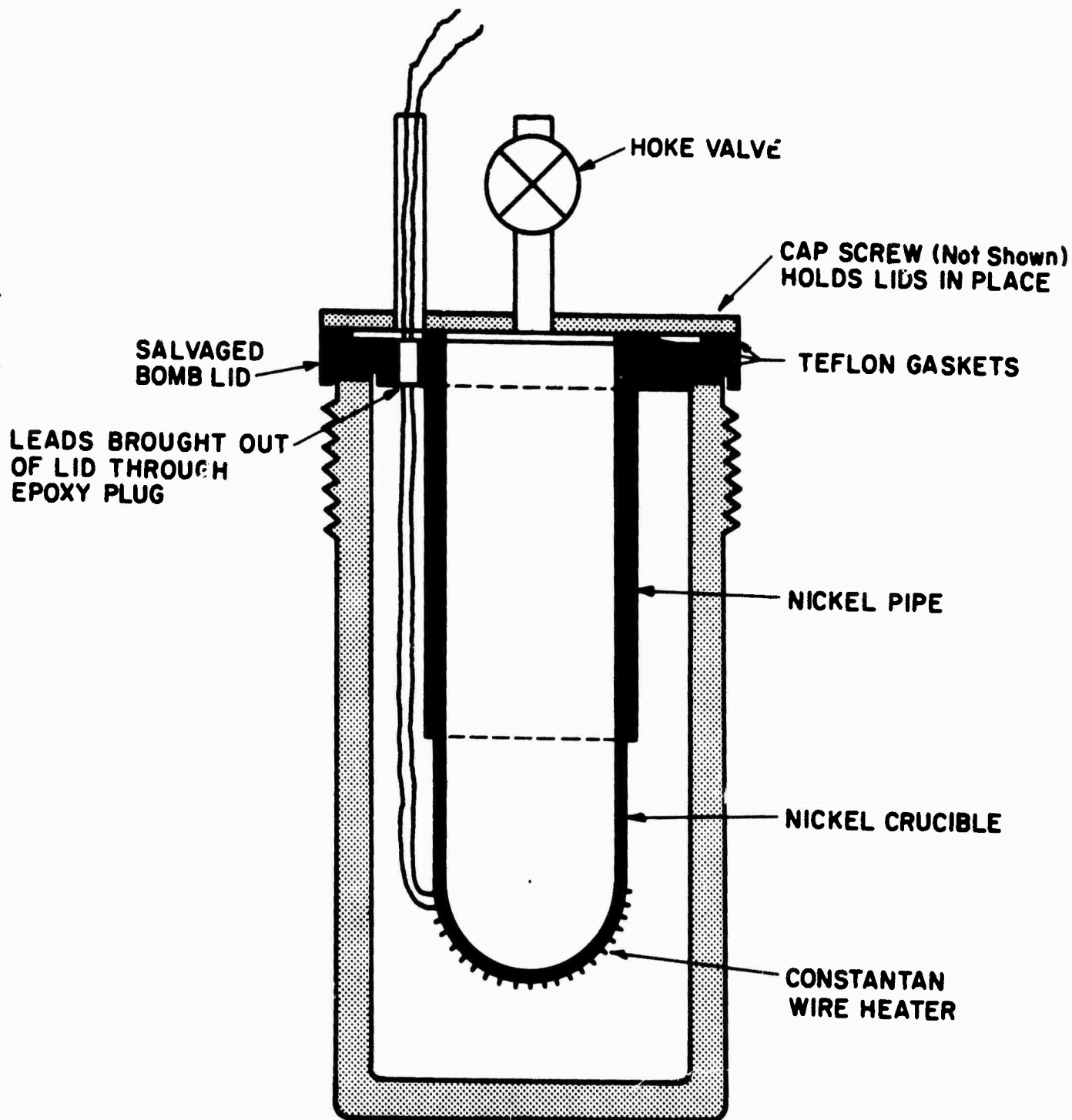
(C) Fig. 2 - Combustion Bomb Modified for Heat
of Decomposition of NF$_4$BF$_4$

(U)   Heater leads were connected to a constant direct current source and, after thermal equilibration and drift rate readings, 1.2 amperes was passed through the 27.5 ohm heater for about 1000 sec.   The current was monitored by means of a standard resistor and potentiometer and the heater resistance was checked by the voltage drop across the heater.   The calorimeter temperature was observed during the heating period and continued through thermal equilibration and final drift period.   The temperature rise corrected for heat leak was calculated by a standard computer program.

(U)   After the decomposition run was completed, the calorimeter was adjusted back to the original initial conditions and the procedure was repeated.   The inner chamber now contained the product gases, so that these calibration runs were made under conditions very similar to the decomposition runs.   Blank runs with the chamber unconditioned and empty gave a different calibration constant, showing the importance of calibrating after, rather than before, the decomposition run itself.   The difference in calibration constant may be related to the interaction of the product gases and the bomb walls; we have noted that BF_3 in a metal vacuum system is strongly absorbed on the surfaces of the system.

(U)   The energy input was calculated from the time, current, and heater resistance.   The temperature rise corrected for heat leak divided into the energy gave the effective calibration constant, E (calor), in cal/°C.

(U)   After the calorimetry was completed, the bomb was attached to a vacuum line and the bomb gases allowed to expand into a known volume.   The final pressure was read on a Wallace & Tiernan dial manometer.   A sample of the gas was then expanded into an infrared cell (AgCl windows) and a spectrum obtained.   A portion of the bomb gas was admitted to a bulb containing a few cc of mercury.   The bulb was shaken to react out F_2 and BF_3, and the remaining gas was examined by mass spectrometry.

c.   Results   (U)

(C)   The effectiveness of this approach was certified by three factors.   The decomposition reaction was assumed to be:

$$NF_4BF_4 \text{ (c)} \rightarrow NF_3 \text{ (g)} + BF_3 \text{ (g)} + F_2 \text{ (g)}$$
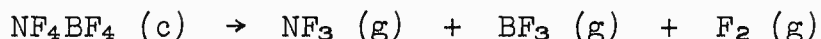
From the sample mass it was possible to calculate the moles of gas expected after decomposition and this could be compared with the amount of gas derived from the measured final pressure, the volume of the bomb and the vacuum system, and the ambient temperature. Excluding one obviously erroneous result, the average moles of gas measured were 95% of theory.   This was considered very satisfactory in view of the neglect of gas imperfection corrections and the tendency for BF_3 to be absorbed on metal surfaces.

(U)   A second factor indicating the assumed decomposition reaction to be correct was the infrared spectrum of the products.   A

-12-

comparison with a spectrum of a mixture of pure BF_3 and NF_3 is given in Figure 3. No unexplained bands are observed in the spectrum of the products. The relative intensities also accord with the expected 1:1 ratio of NF_3 and BF_3.

(C) The third factor lending support to the proposed decomposition reaction was mass spectrometer examination of the bomb gases. A portion of the gaseous products was admitted to an evacuated glass bulb containing a few cc of mercury. The bulb was shaken to react out F_2 and BF_3 (simulated runs showed the BF_3 and F_2 are quantitatively removed by mercury) and the remaining gas analyzed by mass spectrometer. The gas was 95% NF_3 with small amounts of N_2F_4, N_2F_2, CF_4, SiF_4 and O_2. Since these other products may have formed during the sampling process and, in any case, are present in such small amounts, the assumption of decomposition to NF_3, BF_3, and F_2 appears well established. At the same time, the sample of NF_4BF_4 must have been of good purity to agree so well with expectations.

(C) Calorimetric results for the decomposition experiments are given in Table VI. The average value for $\Delta Er/M$ is 184 cal/g with a standard deviation of 7 cal/g. The molecular weight of NF_4BF_4 is 176.805, from which is derived:

$$NF_4BF_4 \ (c) \ \rightarrow \ BF_3 \ (g) \ + \ NF_3 \ (g) \ + \ F_2 \ (g)$$
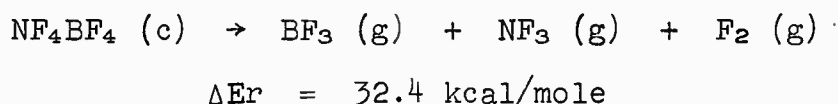
$$\Delta Er \ = \ 32.4 \ kcal/mole$$

Converting to constant pressure conditions:

$$\Delta Hr \ = \ 32.4 \ + \ \Delta nRT$$

$$= \ 34.1 \ kcal/mole$$

The heat of formation of BF_3 is given by Johnson, Feder, and Hubbard (3) as -271.65 kcal/mole and the heat of formation of NF_3 is -31.6 kcal/mole from work by Sinke (4) and Walker (5). Combining these values yields:

$$\Delta Hf_{298}(NF_4BF_4, \ c) \ = \ -337.4 \pm 2.5 \ kcal/mole$$

The uncertainty is taken as twice the standard deviation of the decomposition experiments and does not include uncertainties in the heats of formation of BF_3 and NF_3.

(C) Wilson (6) estimated the heat of decomposition of NF_4BF_4 to be -2 ± 20 kcal/mole and that of NF_4ClO_4 to be -70 ± 20 kcal/mole. The present work indicates NF_4BF_4 to be substantially more stable than Wilson's estimate; correspondingly, the perchlorate may not be as unstable as he predicted. The difficulty of making accurate projections in thermochemistry is attested to by the fact that Wilson's generous limits of error failed to include the experimental result.

-13-
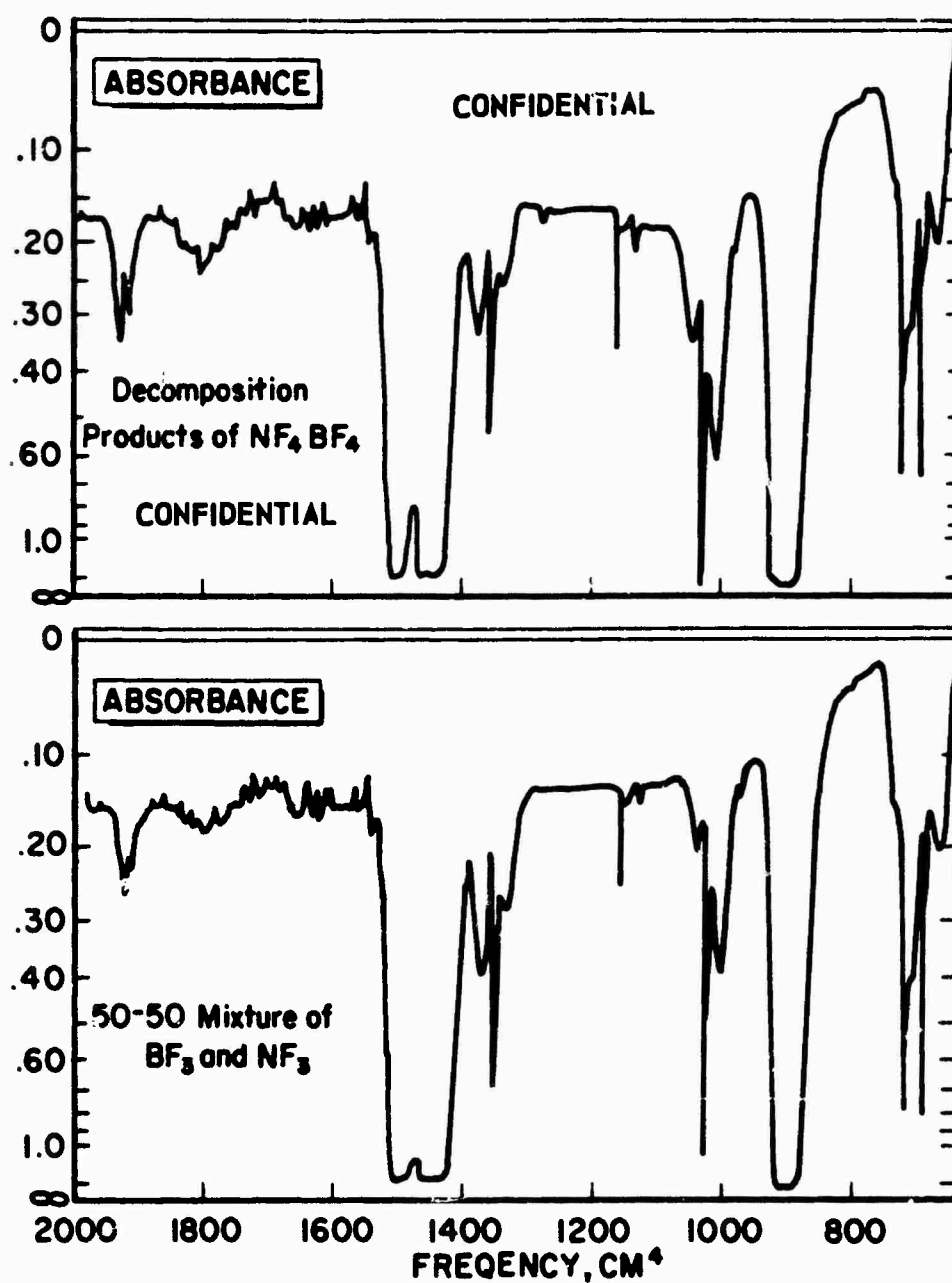
(U) Fig. 3 - Comparison of Infrared Spectra

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Table VI

(C) Heat of Decomposition of NF_4BF_4

Expt. No.	Sample mass, g	Corrected temp. rise, °C	E (calor), cal/°C	Elec. energy, cal.	$\Delta Er/M$, cal/g
5	0.1534	2.93457	3215.9[a]	9460.9	154
6	0.1606	2.93014	3217.2[a]	9458.8	199
7	0.1642	2.93262	3216.7[b]	9464.7	191
8	0.1550	2.93027	3217.0[b]	9457.7	200
10	0.1632	2.92572	3220.7[c]	9451.7	176
11	0.1640	2.92473	3220.6[c]	9448.7	179

[a]One experiment.

[b]Average of two experiments.

[c]Average of three experiments.

B. HEATS OF COMBUSTION OF PBAA AND PBAN (U)

1. Introduction (U)

(U) Samples of the prepolymer materials PBAA and PBAN were
obtained from the American Synthetic Rubber Corporation. These
substances are largely low molecular weight polymers of butadiene
with small amounts of copolymers acrylic acid (PBAA) and acrylo-
nitrile (PBAN). Other additives are also present, as evidenced by
chlorine and sulfur combustion products found in bomb solutions
recovered after heat of combustion experiments. Therefore, re-
sults are reported on the basis of empirical formulas determined
by elemental analysis.

2. Materials (U)

(U) Both PBAA and PBAN are dark, viscous liquids with densi-
ties of 0.92 and 0.96 g/cc, respectively. Elemental analyses for
carbon and hydrogen were made by burning samples in oxygen in a
dry combustion bomb and sweeping the CO_2 and H_2O formed into tubes
packed with Ascarite and magnesium perchlorate, respectively. Ni-
trogen was determined by Kjeldahl analysis and sulfur by standard
peroxide fusion and determination of sulfate. The oxygen content
was measured by neutron activation analysis. In addition, solu-
tions recovered from the bomb after calorimetric combustion experi-
ments were analyzed for chloride and sulfate. Analytical data are
collected in Table VII and are compared with the selected empirical
compositions.

Table VII

Analytical Data for PBAA and PBAN (U)

	C	H	O	S	N	Cl
				Element		
PBAA						
% Present	85.34	11.00	2.2	1.0	0.3	--
Estimated Uncertainty	±0.05	±0.05	±0.1	±0.05	±0.1	--
Method	Combustion		Neutron activation	Peroxide fusion	Kjeldahl	--
Calculated for $C_{7.11006}H_{10.91302}O_{0.41376}S_{0.03118}N_{0.02142}$	85.40	11.00	2.30	1.00	0.30	--
PBAN						
% Present	82.80	10.30	2.2	1.0	3.25	0.50
Estimated Uncertainty	±0.05	±0.05	±0.1	±0.05	±0.1	±0.1
Method	Combustion		Neutron activation	Peroxide fusion	Kjeldahl	Chloride in bomb solutions.
Calculated for $C_{6.89359}H_{10.21855}O_{0.13751}N_{0.22846}S_{0.03119}Cl_{0.01410}$	82.80	10.30	2.20	1.00	3.20	0.50

3. Equipment and Procedure   (U)

(U)   A platinum-lined combustion bomb and rotating bomb calorimeter were employed.   Standard heat of combustion procedures were followed.   Samples were burned in open crucibles with only a cotton thread fuse as auxiliary material.

4. Results   (U)

(U)   Results of the calorimetric experiments were calculated by standard computer programs based on the outline of Hubbard, Scott, and Waddington (7).   Constant factors used in the calculations are given in Tables VIII and IX and typical experimental runs are outlined in Table X.   Individual runs and overall average are given in Table XI.

(U)   The average result for PBAA refers to the reaction:

$C_{7.11006}H_{10.91302}O_{0.14376}S_{0.03119}N_{0.02142}$ (1) + 9.81322 O_2 (g) →

7.11006 CO_2 (g) + 5.42532 H_2O (1) + 0.03119 H_2SO_4 (in 400 H_2O) +

0.01071 N_2 (g)
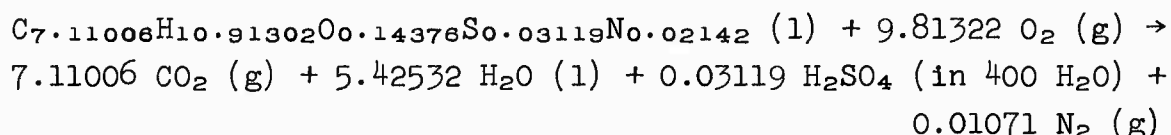
$$\Delta E\overset{\circ}{c}_{298} = -1036.09 \text{ kcal/100 g}$$

Correcting to constant pressure conditions:

$$\Delta H\overset{\circ}{c}_{298} = \Delta E\overset{\circ}{c}_{298} + \Delta nRT$$
$$= -1036.09 - 1.60$$
$$= -1037.69 \text{ kcal/100 g}$$

With heats of formation of CO_2 (g), H_2O (1), and H_2SO_4 (400 H_2O) from NBS Technical Note 270-3, there is derived for PBAA:

$$\Delta H\overset{\circ}{f}_{298}(\text{PBAA, 1}) = -8.28 \text{ kcal/100 g}$$

(U)   The average result for PBAN refers to the reaction:

$C_{6.89359}H_{10.21855}O_{0.13751}S_{0.03119}N_{0.22846}Cl_{0.01410}$ (1) + 9.42273 O_2 (g) →

6.89359 CO_2 (g) + 5.07104 H_2O (1) + 0.03119 H_2SO_4 (400 H_2O) +

0.01410 HCl (1000 H_2O) + 0.11423 N_2 (g)
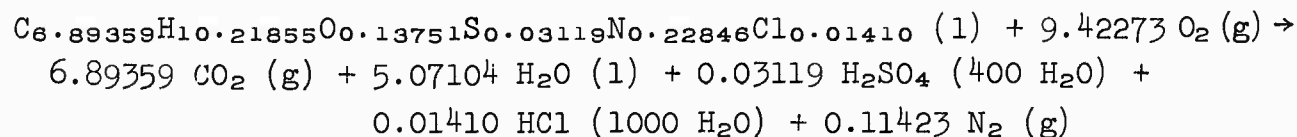
$$\Delta E\overset{\circ}{c}_{298} = -999.84 \text{ kcal/100 g}$$

Correcting to constant pressure conditions:

$$\Delta H\overset{\circ}{c}_{298} = -999.84 - 1.43$$
$$= -1001.27 \text{ kcal/100 g}$$

-17-

Table VIII

Constant Factors for Calculation of Heat
of Combustion of PBAA^a (U)

Formula of Compound	$C_{7.11006}H_{10.91302}O_{0.14376}S_{0.03118}N_{0.02148}$
Formula of Fuse	$CH_{1.8}O_{0.9}$
Density of Compound, g/cc at 25°C	0.9195
Density of Fuse, g/cc	1.5
Bomb Volume, liter	0.349
Initial Oxygen Pressure at 25°C, atm	30.3
Reference Temperature, °C	25
$(\partial E/\partial P)_t$ of Compound, cal/g/atm	(-0.00614)
ΔE_c° of Fuse, kcal/mole	-111.70
Cp of Compound, cal/g/°C	(0.5)
Cp of Fuse, cal/g/°C	(0.4)
E(calor), cal/°C	3427.2

^{a}Quantities in parentheses are estimated.

-18-

Table IX

Constant Factors of Calculation of Heat of Combustion of PBAN[a] (U)

Formula of Compound	$C_{6.89359}H_{10.21855}O_{0.13751}S_{0.03119}N_{0.22848}Cl_{0.01410}$
Formula of Fuse	$CH_{1.8}O_{0.9}$
Density of Compound, g/cc at 25°C	0.961
Density of Fuse, g/cc	1.5
Bomb Volume, liter	0.349
Initial Oxygen Pressure at 25°C, atm	30.3
Reference Temperature, °C	25
$(\partial E/\partial P)_t$ of Compound, cal/g/atm	(-0.00614)
ΔE°_c of Fuse, kcal/mole	-111.70
Cp of Compound, cal/g/°C	(0.5)
Cp of Fuse, cal/g/°C	(0.4)
E(calor), cal/°C	3427.2

[a]Quantities in parentheses are estimated.

Table X

Summary of Typical Calorimetric Experiments
for PBAA and PBAN (U)

	PBAA	PBAN
m(compd.), g	0.666819	0.682194
m'(fuse), g	0.002560	0.002400
ηi(H_2O)	0.05534	0.05534
t_i, °C	22.96666	22.96673
Δt_f, °C	25.05055	25.02575
Δt_{corr}, °C	0.06691	0.06722
E^i(cont.), cal/°C	5.35	5.35
E^f(cont.), cal/°C	5.69	5.66
E(calor), cal/°C	3427.20	3427.20
ΔE_{ign}, cal	0.37	0.36
ΔE(cor. to std. states), cal	2.64	2.65
$-m'\Delta E8/M$(fuse), cal	10.14	9.50
$m\Delta E8/M$(compd.), cal	-6908.82	-6821.18
$\Delta E8/M$(compd.), cal/g	-10360.19	-9998.9

With auxiliary heats of formation from NBS Technical Note 270-3:

$$\Delta Hf_{298}(\text{PBAN, l}) = -0.70 \text{ kcal/100 g.}$$

Table XI

(U)   Heats of Combustion of PBAA and PBAN

Expt. No.	$-\Delta E_c^\circ$ (kcal/100 g of PBAA)	$-\Delta E_c^\circ$ (kcal/100 g of PBAN)
1	1036.49	999.90
2	1036.21	999.73
3	1035.69	999.89
4	1035.97	999.99
5	1036.09	999.56
6	--	999.96
Avg.	-1036.09 kcal/100 g of PBAA	-999.84 kcal/100 g of PBAN
Std. Deviation	0.13	0.07

C.   HEATS OF COMBUSTION OF ELF-100 AND ELF-101   (U)

1.   Introduction   (U)

(C)   ELF-100 and ELF-101 are code designations for two C-H-N compounds synthesized at Esso Research and Engineering Company. Work on the heat of combustion is reported here for aminoethyl-aziridine, $C_4H_{10}N_2$ (ELF-100), and methyldiazabicyclooctane, $C_7H_{14}N_2$ (ELF-101).

2. Materials   (U)

(U)   Correspondence from Esso Research and Engineering Company stated the materials were "analytically pure as attested to by C-H-N analysis, NMR, and IR." The samples were liquids of low vapor pressure but appreciable reactivity with respect to absorption of water and CO_2.

(U)   A check on these samples was made by neutron activation analysis for oxygen. Results indicated 0.56 and 0.25 weight percent oxygen in the ELF-100 and ELF-101, respectively. Karl Fischer analysis for water in these samples gave erratic results, possibly due to interference by the samples themselves.

(U)   Heat of combustion measurements, to be described in a later section, indicated the ELF-101 sample was decomposing in some way. Therefore, another batch of ELF-101 was obtained from Houdry Chemical Company (also the source of the original Esso sample). The Houdry material was distilled and a center cut had a purity of 99.6 mole % by freezing curve analysis. The initial freezing point of

this cut was -60.7°C. Freezing curves on a less pure cut showed an initial freezing point of -61.8°C, but the entire curve did not reflect the lower purity. Thus, there is some doubt about the validity of the freezing curve technique in this case. Karl Fischer analysis for water on the cut freezing at -60.7°C showed less than 0.1% with no evidence of interference. Any impurities are therefore assumed to be organic in nature, hopefully with heats of combustion similar to ELF-101 itself.

(U) Assessments of the accuracy of the calorimetry on these samples must take into account the above described uncertainties about sample purity.

3. Equipment (U)

(U) A typical rotating bomb calorimeter and a platinum-lined combustion bomb were employed.

4. Procedure (U)

(U) Tests showed that samples enclosed in Mylar film picked up weight when exposed to the atmosphere, presumably by diffusion of moisture through the plastic. Samples were therefore loaded in a dry atmosphere into thin walled glass ampoules which were sealed off. The weighed ampoules were placed in a platinum crucible and a small weighed amount of paraffin oil was added. The bomb was charged in the usual way and fired electrically. The paraffin oil ignited and the heat burst the sample ampoule, allowing its contents to burn completely. After the calorimetry the bomb was rinsed out and the solution titrated for HNO_3 formation.

5. Results (U)

(C) Results were calculated by computer using standard procedures. Constant factors employed in the calculations are given in Table XII, and data for the individual experiments in Tables XIII, XIV, and XV. The average result for ELF-100 from Table XIV and a molecular weight of 86.1377 yields $\Delta Ec_{298}^{o} = -729.57 \pm 0.51$ kcal/mole for the constant volume process:

$$C_4H_{10}N_2 \ (1) + 13/2 \ O_2 \ (g) \rightarrow CO_2 \ (g) + 5 \ H_2O \ (1) + N_2 \ (g).$$
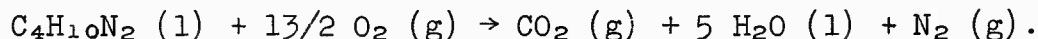
Calculating to constant pressure conditions gives:

$$\Delta Ec_{298}^{o} = -730.46 \pm 0.51 \ \text{kcal/mole}$$

from which is derived:

$$\Delta Hf_{298}^{o} \ (1) = +12.68 \pm 0.51 \ \text{kcal/mole}$$

The error is twice the standard deviation of the experiments and does not include any uncertainty due to impurities.

(U) The results for ELF-101 (Sample I from Esso) show a trend with time as illustrated in Figure 4. Apparently some process such as isomerization, polymerization, or decomposition is taking place which results in a steadily decreasing heat of combustion.

Table XII

(C) Constant Factors for Heat of Combustion Calculations

Empirical formula, ELF-100	$C_4H_{10}N_2$
Empirical formula, ELF-101	$C_7H_{14}N_2$
Empirical formula, paraffin oil	$CH_{1.8374}$
Empirical formula, Mylar film	$C_{10}H_8O_4$
Empirical formula, fuse	$CH_{1.8}O_{0.9}$
Density of ELF-100, g/cc	0.986
Density of ELF-101, g/cc	0.899
Density of paraffin oil, g/cc	0.89
Density of film, g/cc	1.38
Density of fuse, g/cc	1.5
Bomb volume, liter	0.347
Initial oxygen pressure, atm	30.3
Initial water, liter	0.001*
Reference temperature, °C	25.00
$(\delta E/\delta P)_T$ of ELF-100 and ELF-101, cal/g/atm	-.00189
$(\delta E/\delta P)_T$ of paraffin oil, cal/g/atm	-.00614
$(\delta E/\delta P)_T$ of film, cal/g/atm	-.00080
ΔE_c° of film, kcal/mol	-104.89
ΔE_c° of fuse, kcal/mol	-111.7
Cp of ELF-100 and ELF-101, cal/g/°C	0.5
Cp of oil, cal/g/°C	0.5
Cp of film, cal/g/°C	0.315
Cp of fuse, cal/g/°C	0.4
E (calor) for ELF compounds, cal/°C	3414.71
E (calor) for paraffin oil, cal/°C	3427.20

*Exp. 9B - 0.002 liter.
 Exp. 10 - 0.010 liter.

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Table XIII

(U) Heat of Combustion Experiments for Paraffin Oil

Experiment No.

Parameter	1	2	3	4	5
Paraffin oil, g	0.617860	0.629315	0.635555	0.623490	0.620375
Fuse, g	0.003105	0.001762	0.002325	0.002290	0.002050
t_i, °C	22.966760	22.966750	22.966740	22.966700	22.966670
t_f, °C	25.024040	25.057450	25.077540	25.039940	25.029350
Δt_{corr}, °C	0.072730	0.070930	0.069900	0.071090	0.071430
E_c/M, cal/g	-10987.70	-10988.06	-10990.57	-10990.45	-10986.89

Parameter	6	7	8	9	10
Paraffin oil, g	0.573732	0.575125	0.570325	0.573465	0.556385
Polyester film, g	0.101800	0.098865	0.100370	0.090380	0.099555
Fuse, g	0.003715	0.002800	0.003395	0.003315	0.002985
t_i, °C	22.966720	22.966740	22.966720	22.966710	23.004490
t_f, °C	25.045280	25.041740	25.031040	25.024170	25.024730
Δt_{corr}, °C	0.072110	0.070510	0.072070	0.070910	0.07406
$\Delta E_c/M$, cal/g*	-10991.19	-10986.86	-10987.20	-10988.66	-10989.65

*$\Delta E_c/M$ (average) = -10988.7 cal/g.

-24-

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Table XIV

Heat of Combustion Experiments for ELF-100 (U)

Parameter	Experiment Number					
	1	2	3	4	5	6
ELF-100, g	0.65972	0.63410	0.42972	0.59791	0.428383	0.57337
Paraffin oil, g	0.11292	0.19047	0.31966	0.19847	0.40557	0.30010
Fuse, g	0.00271	0.002720	0.00285	0.002196	0.003364	0.002352
Mole of HNO_3(x10^3) final	1.197	1.164	0.899	1.090	0.888	1.100
Mass of glass, g	0.1321	0.1593	0.1133	0.1272	0.0683	0.1349
Mass of added Pt, g	51.0461	51.0461	51.0279	51.0279	51.0279	51.0279
t_i, °C	22.91021	22.71656	22.86632	22.84750	22.56786	22.58572
t_f, °C	24.98126	24.97797	25.02991	25.03803	25.00303	25.03548
Δt corr. °C.	0.06481	0.06884	0.06210	0.06231	0.05966	0.06182
$-\Delta E_c^\circ/M$, cal/g	8463.50	8469.52	8473.32	8469.14	8481.66	8462.16

Average: $-\Delta E_c^\circ/M$ = 8469.9 cal/g

Std. Dev. = ±3 cal/g

Table XV

(U) Heat of Combustion Experiments for ELF-101 (Sample I)

Parameter	Experiment Number			
	1	2	3	4
ELF-101, g	0.526429	0.623251	0.481497	0.464134
Paraffin oil, g	0.213894	0.173300	0.245916	0.266040
Fuse, g	0.003003	0.002439	0.003155	0.003253
Mole of HNO_3 (x10^3) final	0.703	0.738	0.730	0.730
Mass of glass, g	0.1300	0.1398	0.0944	0.05940
Mass of Pt added, g	51.0279	51.0279	51.0279	51.0279
t_i, °C	22.76638	22.83500	22.87885	22.94780
t_f, °C	24.92091	25.09520	24.99467	25.08134
Δt_{corr}, °C	0.07200	0.05774	0.05815	0.05940
$-\Delta Ec/M$, cal/g	9,005.23	8,981.75	8,936.95	8,915.42
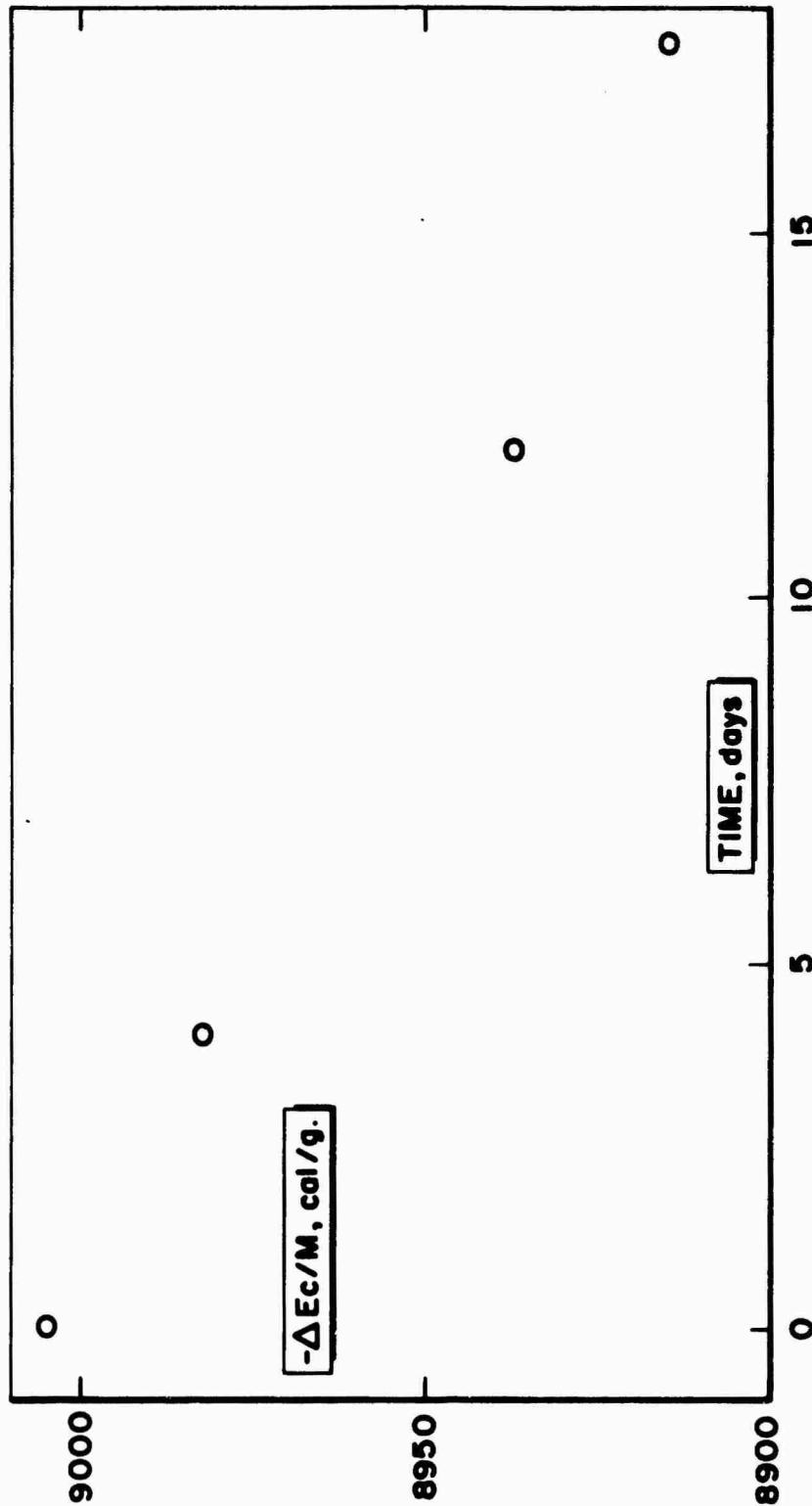
(U) Fig. 4 - Variation of Heat of Combustion
of ELF-101 (Sample I) with Time

(U) The results for ELF-101 (Sample II, purified at Dow) show good precision (Table XVI). This sample was frozen shortly after purification and was kept frozen in sealed glass ampoules until just before the combustion experiments. It is not known, there-fore, whether Sample II would have shown decreasing ΔHc if it had been allowed to stand at room temperature.

(C) The average result for ELF-101 from Table XVI and a molecular weight of 126.203 yields $\Delta Ec^0_{298} = -1138.07$ kcal/mole for the constant volume process:

$$C_7H_{14}N_2 \text{ (l)} + 21/2\ O_2 \text{ (g)} \rightarrow 7\ CO_2 \text{ (g)} + 7\ H_2O \text{ (l)} + N_2 \text{ (g)}$$

Converting to constant pressure conditions:

$$\Delta Hc^0_{298} = -1139.55 \pm 0.33 \text{ kcal/mole}$$

from which is derived:

$$\Delta Hf^0_{298} \text{ (l)} = 2.99 \pm 0.33 \text{ kcal/mole}.$$

As for ELF-100, the error does not include uncertainty in sample purity.

D. HEAT OF COMBUSTION OF METHYLENE BISOXYAMINE (C)

1. Introduction (U)

(C) A sample of methylene bisoxyamine, $CH_6O_2N_2$, Code DOA, was received from Rocket Propulsion Laboratory at Edwards Air-Force Base. The heat of formation was determined by standard oxygen combustion calorimetry.

2. Material (U)

(U) Correspondence from AFRPL informed us that DOA is flam-mable, has an impact sensitivity of 70 kg-cm, and has a vapor pressure of 1 mm at 33°C. It must be handled in a dry box and is decomposed catalytically by a number of substances. Purity is 99.1% (method used was not specified). Because only a small amount of sample was available, no attempts at analysis or purification were made at Dow.

(U) Ethylene glycol containing a little water was used as a diluent for DOA. The heat of combustion of the glycol was deter-mined in separate experiments.

3. Equipment (U)

(U) A standard rotating bomb combustion calorimeter and a platinum-lined combustion bomb were employed.

Table XVI

(U) Heat of Combustion Experiments for ELF-101 (Sample II)

Parameter	Experiment Number				
	1	3	5	6	7
ELF-101, g	0.60754	0.76309	0.64369	0.37457	0.74312
Paraffin oil, g	0.19289	0.11065	0.17287	0.35408	0.11565
Fuse, g	0.00204	0.00200	0.00187	0.00188	0.00233
Mole of $HNO_3(\times 10^3)$, final	0.900	1.130	0.985	0.729	1.090
Mass of glass, g	0.10	0.17	0.11	0.06	0.14
Mass of added Pt, g	58.97	58.97	58.97	58.97	58.97
t_i, °C	22.99722	22.99712	22.99748	22.99742	22.99668
t_f, °C	25.22741	25.37535	25.25879	25.13015	25.33848
Δt_{corr}, °C	0.05535	0.04725	0.05041	0.04745	0.03637
$-\Delta E_c°/M$, cal/g	9,016.19	9,020.99	9,015.80	9,015.17	9,020.75

Mean: $-\Delta E_c°/M = 9{,}017.8$ cal/g .

Std. Dev. $= 1.3$ cal/g.

4. Procedure (U)

(U) Preliminary experiments showed DOA detonated to incomplete combustion products when ignited in a platinum crucible in 30 atm of oxygen. Suitable moderation of the reaction was achieved by burning a 50-50 mixture of DOA and ethylene glycol as follows.

(U) A long, narrow polyethylene bag was fabricated from polypropylene film and weighed. A metal clamp was placed across the middle of the bag and the assembly weighed. The clamped bag was taken into a dry box and an appropriate amount of DOA added to one side which was then sealed. The loaded bag was removed from the dry box and weighed. An appropriate amount of ethylene glycol was added to the other side of the bag, and the bag was sealed and weighed. If weighing data showed no leaks existed, the clamp was removed and the two liquids were mixed in the bag. The heat of combustion was then measured by the usual techniques.

(U) The heat of combustion of the ethylene glycol was also measured in the same apparatus. The conditions for the glycol experiments (such as weighing time) were kept as nearly as possible identical to the DOA-glycol experiments to eliminate systematic errors.

(U) The heat of mixing of DOA and ethylene glycol was measured in a Beckman microcalorimeter.

5. Results (U)

(U) Constant factors used in the computer program for data reduction are given in Table XVII. Typical experimental data are given in Table XVIII and individual experiments in Table XIX.

(C) To the average result of Table XIX is added the heat of mixing of 5.0 cal/g to give $-\Delta E_c/M = 3524.6$ cal/g. The molecular weight of methylene bisoxamine is 78.071 which yields:

$$\Delta E_{c}^{\circ}{}_{298} = -275.17 \text{ kcal/mole}$$

for the reaction:

$$CH_6O_2N_2 \text{ (c)} + 1.5 \text{ } O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 3 \text{ } H_2O \text{ (l)} + N_2 \text{ (g)}.$$
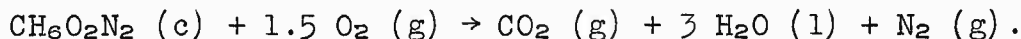
Calculating to constant pressure conditions:

$$\Delta H_{c}^{\circ}{}_{298} = -274.88 \pm 0.36 \text{ kcal/mole}.$$

Auxiliary data for CO_2 and H_2O then yield for methylene bisoxyamine:

$$\Delta H_{f}^{\circ}{}_{298} \text{ (l)} = -24.12 \pm 0.36 \text{ kcal/mole}.$$

The uncertainty does not include any error due to impurities in the sample, but is only the calorimetric uncertainty for the sample as submitted.

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Table XVII

(C)   Constant Factors in Calorimetry of Methylene
Bisoxyamine (Code DOA)[a,b]

Empirical formula, DOA	$CH_6O_2N_2$
Empirical formula, glycol	$C_2H_6O_2$
Density of DOA, g/cc	1.100
Density of glycol, g/cc	1.115
Bomb volume, liter	0.347
Initial oxygen pressure, atm	30.3
Initial water in bomb, g	1.0
Reference temperature, °C	25.00
$(\partial E/\partial P)_T$ of DOA, cal/g/atm	(-0.0030)
$(\partial E/\partial P)_T$ of glycol, cal/g/atm	-0.00397
Cp of DOA, cal/g/°C	(0.50)
Cp of glycol, cal/g/°C	0.5'7
E (Calor), cal/°C	3414.70

[a]Quantities in parentheses are estimated.

[b]For polypropylene film and cotton fuse see
Table I, this report.

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Table XVIII

Combustion Experiments on Ethylene Glycol (U)

Parameter	Experiment No.					
	1	2	5	8	9	10
Glycol mass, g	1.35526	1.37654	1.36454	1.35675	1.36230	1.36650
Film mass, g	0.07973	0.07098	0.09712	0.10866	0.12768	0.11744
Fuse mass, g	0.00256	0.00263	0.00283	0.00328	0.00312	0.00294
t_i, °C	22.96672	22.96672	22.96672	22.96674	22.96685	22.96667
t_f, °C	25.08991	25.08810	25.15761	25.18241	25.24849	25.22189
Δt_{corr}, °C	0.05735	0.05612	0.05409	0.05210	0.04846	0.04979
E_i, cal/°C	6.210	6.220	6.194	6.193	6.202	6.201
E_f, cal/°C	6.736	6.744	6.739	6.747	6.776	6.766
ΔE_{corr} std. states, cal	3.510	3.533	3.616	3.647	3.749	3.714
$-\Delta E_c^\circ/M$, cal/g	4552.9	4551.2	4557.8	4555.9	4558.0	4558.0

Average $-\Delta E_c^\circ/M$ = 4555.6 cal/g

Std. Dev. = 1.2 cal/g

-32-

Table XIX

(C) Combustion Experiments on Methylene Bisoxyamine (Code DOA)

Parameter	Experiment Number					
	3	5	6	7	10	11
DOA mass, g	0.43637	0.46426	0.44164	0.44883	0.43688	0.45151
Glycol mass, g	0.83409	0.84072	0.84071	0.83940	0.84715	0.86046
Film mass, g	0.11678	0.10238	0.11076	0.11950	0.13251	0.13388
Fuse mass, g	0.00341	0.00258	0.00264	0.00243	0.00292	0.00278
t_i, °C	22.96670	22.96678	22.96676	22.96666	22.96673	22.96676
t_f, °C	24.97803	24.96921	24.97617	25.00234	25.04183	25.07506
Δt_{cor}, °C	0.06491	0.06540	0.06943	0.06333	0.06087	0.05651
E_i, cal/°C	5.989	6.000	5.992	6.023	6.024	5.984
E_f, cal/°C	6.639	6.646	6.640	6.681	6.695	6.666
ΔE cor. std. states, cal	3.101	3.110	3.098	3.149	3.197	3.268
ΔE_{HNO_3}, cal	10.589	11.556	11.598	10.827	12.215	12.636
$-\Delta E_c°/M$, cal/g	3524.1	3526.6	3519.6	3511.0	3516.6	3519.6

Average $-\Delta E_c°/M$ = 3519.6 cal/g

Std. Dev. = 2.3 cal/g

E. HEAT OF FORMATION OF CF_3NF_2 (U)

1. Introduction (U)

· (U) Difluoroaminotrifluoromethane, CF_3NF_2, is the last member of the series of $-NF_2$ substituted fluoromethanes that this laboratory has studied to determine enthalpies of formation. Of secondary interest was the C-N and N-F bond energy as compared to the other members. (To date, no heat of formation has been reported in the literature for this compound.)

2. Preparation and Characterization of Sample (U)

(U) Difluoroaminotrifluoromethane was synthesized by Mrs. Linda Calhoun of the Chemicals Department of The Dow Chemical Company by the method of Ruff (8). This involves a catalytic fluorination of potassium thiocyanate at dry ice temperature in a Monel cylinder. The reaction is shown below:
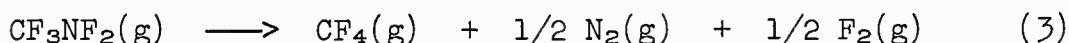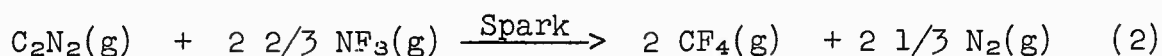
$$KSCN + 6F_2 \xrightarrow[\text{KF Catalyst}]{-78°C} KF + SF_6 + CF_3NF_2 \qquad (1)$$
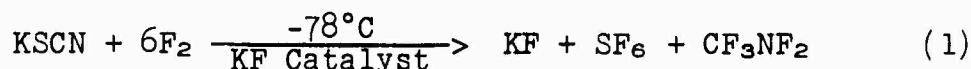
The equimolar mixture of SF_6 and CF_3NF_2 was separated by low temperature distillation in a modified gas chromatograph apparatus.

(U) The infrared spectrum of CF_3NF_2 agreed well with that of Pearson and Dresdner (9); however, mass spectroscopy indicated 0.5 mole percent of residual SF_6 that was difficult to remove by further distillation. Molecular weight measurements by gas density agreed with theory (121 g/mole) within limits of error. The purity of the gas was thus taken to be 99.5% and a correction made for the presence of the inert SF_6.

3. Calorimetric Reaction (U)

(U) Initial experiments to find a reaction suitable for a heat measurement indicated that CF_3NF_2 would not rearrange to CF_4 and N_2 upon sparking the gas, as had been the case for $CF_2(NF_2)_2$, $CF(NF_2)_3$ and $C(NF_2)_4$ (10). A mixture of CF_3NF_2, NF_3 and C_2N_2 did, however, give the desired reaction, the NF_3-C_2N_2 mixture acting as a trigger. The system consisted of a Hewlett-Packard electronic quartz resonator thermometer (Model 2801 A) which resolved temperatures to ±0.0001°C. This unit was linked to an IBM 1800 computer for automatic acquisition and reduction of the raw data. The IBM computer was in turn linked to a Burroughs 5500 computer which calculated the "corrected temperature change" (7). Experiments carried out in this manner are virtually 100% automated with the added advantage that the computers do all of the data handling, transcribing and processing. Comparisons of the new system with the older version showed them to be identical within experimental error.

(U) Electrical energy calibrations were used for the CF_3NF_2 work. Fourteen experiments carried out over the range 24°-25°C. gave a value of $E(calor) = 3,199.6$ cal/deg with a standard deviation of the mean (σ) equal to ±0.3 cal/deg. A series of data for this reaction was available, as well as techniques for purification of C_2N_2 and NF_3 (11). The calorimetric reaction is indicated below as separated into the two simultaneously occurring steps:

$$C_2N_2(g) + 2\,2/3\,NF_3(g) \xrightarrow{Spark} 2\,CF_4(g) + 2\,1/3\,N_2(g) \quad (2)$$

$$CF_3NF_2(g) \longrightarrow CF_4(g) + 1/2\,N_2(g) + 1/2\,F_2(g) \quad (3)$$

Reaction (2) accounted for about 80% of a typical gross heat of 1,200 cal. This ratio was necessary because of the problem of working with cyanogen in accurately weighable quantities. In practice the reaction was run with a small excess of NF_3 which was dissociated to the elements. This side reaction necessitated a small correction (4,5).

4. Calorimeter System (U)

(U) A previously described Dickinson-type 25°C isothermal shield calorimeter and nickel combustion bomb were used for this project (12). Calibrations by benzoic acid combustions were run as a comparison with the electrical inputs. These agreed to within 1.5 cal/deg, but had more scatter than the electrical inputs. The electrical calibrations were taken as most definitive for this bomb system.

5. Experimental Procedure (U)

(U) The nickel bomb (Lab. Desig. NIB-2) was passivated by carrying out several N_2F_4-C_2N_2 reactions. Between reactions the bomb was kept under vacuum and opened only in a dry nitrogen glove box. After four explosion reactions the interval surfaces of the bomb were noticeably glazed with NiF_2.

(U) A determination first involved fitting a weighed nickel fuse between the electrodes of the bomb. The bomb was then evacuated to less than five microns pressure. CF_3NF_2, contained in a 10 ml Hoke cylinder, was metered into the bomb to a pressure of about 250 mm Hg. The bomb valve was then closed and the CF_3NF_2 in the manifold condensed back into the small cylinder. The mass of CF_3NF_2 charged to the bomb was determined by weighing the sample cylinder before and after loading. Cyanogen and NF_3 were then added to the bomb using the same procedure. The bomb was then placed in the calorimeter and the reaction initiated by discharging a standardized capacitor across the nickel fuse wire.

(U)   After each heat measurement the bomb was attached to the vacuum line for gas sampling. Any excess F_2 was removed using mercury and the products checked by mass spectral analysis.   In all determinations CF_4 and N_2 were found (plus SF_6) in the correct ratio as predicted by the masses of starting materials. The bomb was finally opened in the dry box and the unburned pieces of nickel fuse recovered. These were cleaned and weighed to determine the net amount burned to NiF_2. Data for this correction were available (13).

6. Results   (U)

(U)   Table XX lists the results of three experiments. Two other measurements were discarded because of wide variations that could not be explained. The mass of CF_3NF_2 was corrected for 0.6 wt.% SF_6. Qv is the gross heat equal to E(calor) $\Delta\theta$, where $\Delta\theta$ is the "corrected temperature change." The following four columns list the corrections in calories as described previously, and $\Delta Er/M$ is the internal energy change at constant volume in calories per gram of CF_3NF_2.

Table XX

Heat of Reaction Data for CF_3NF_2 (U)

Run No.	CF_3NF_2, g	Qv, Cal	Corrections in Cal				$\Delta Er/M$*, cal/g
			C_2N_2-NF_3	NF_3	NiF_2	Ig'n	
1	0.5464	-1,246.9	998.6	-0.7	0.8	0.3	-453.7
3	0.6016	-1,294.9	1,024.4	-1.3	1.2	0.4	-449.1
4	0.5825	-1,273.1	1,014.5	-5.9	0.7	0.3	-452.4
						Avg.	-451.7

*Standard dev. of mean = ±1.3 cal/g.

(U)   The standard state enthalpy of reaction per mole of CF_3NF_2 is calculated as follows:

$$\Delta Er = -54.66 \pm 0.3 \text{ kcal/mole}$$

$$\Delta nRT = 0.59 \text{ kcal}$$

$$\Delta Hr = -54.07 \pm 0.3 \text{ kcal/mole}$$

Taking $\Delta Hf(CF_4, g) = -223.0 \pm 0.2$ kcal/mole (10) there is derived:

$$\Delta Hf^{\circ}_{298}(CF_3NF_2, g) = -168.9 \pm 0.5 \text{ kcal/mole}$$

7. Bond Energies (U)

(U) It is interesting to compare this experimental result with predictions from bond energy terms. The bond energy values adopted by Sinke et al. (10) are adopted here: E(C-F) = 117.5, E(N-F) = 67.1, and E(C-N) = 65.2 kcal, and enthalpies of atomization of the elements C = 171.3, F = 18.9, and N = 113.0 kcal. This yields for CF_3NF_2 a $\Delta Hf(g)$ = -173.1 kcal/mole. As discussed by Sinke et al. (10), a correction must be applied because the resonance energy of the -CF_3 group is less than that of CF_4. This correction, according to references cited by Sinke et al. (10), is +3.6 kcal/mole, and the final calculated value is $\Delta Hf(g)$ =-169.5 kcal/mole, in excellent agreement with the experimental result.

(U) Heats of formation of the series $CF_x(NF_2)_{4-x}$ are plotted as a function of x in Figure 5. Within a few kcal/mole, a linear relationship exists for this series of compounds.

F. HEAT OF FORMATION OF AQUEOUS HYDRAZINE DIHYDROCHLORIDE AND
CHLORINE PENTAFLUORIDE (U)

1. Introduction (U)

(U) Several years ago the heat of formation of chlorine pentafluoride was determined in this laboratory by reaction with aqueous hydrazine dihydrochloride (14, 15, 16). Since that time, Howard and Skinner (17) published data on the thermochemistry of hydrazine which indicated the heat of formation of aqueous hydrazine dihydrochloride could be appreciably less negative than the value assumed for correcting the ClF_5 work. We have, therefore, completed appropriate heat of mixing experiments which serve to better define the heat of formation of $N_2H_6Cl_2$ (aq) and of ClF_5 (g). The results for $N_2H_6Cl_2$ are also significant in the combustion calorimetry of organic chlorine compounds and will be discussed in this connection.

2. Equipment and Procedure (U)

(U) For the heat of mixing experiments, a static combustion calorimeter was adapted by adding an acrylate plastic chamber suspended from the lid of the bucket ordinarily used to hold the combustion bomb. As shown in Figure 6, an acrylate rod, fitted with double pistons which closely fit the chamber, extended out of the calorimeter. The chamber was charged with the appropriate reagent or solution, while the bucket was filled with the second component. After equilibration in the calorimeter and taking of drift rate readings, the rod was pushed down, allowing the two solutions to mix completely. Final drift readings completed the calorimetry. The usual thermistor-resistance bridge combination was used for temperature measurement and the corrected temperature rise was calculated by means of a computer.
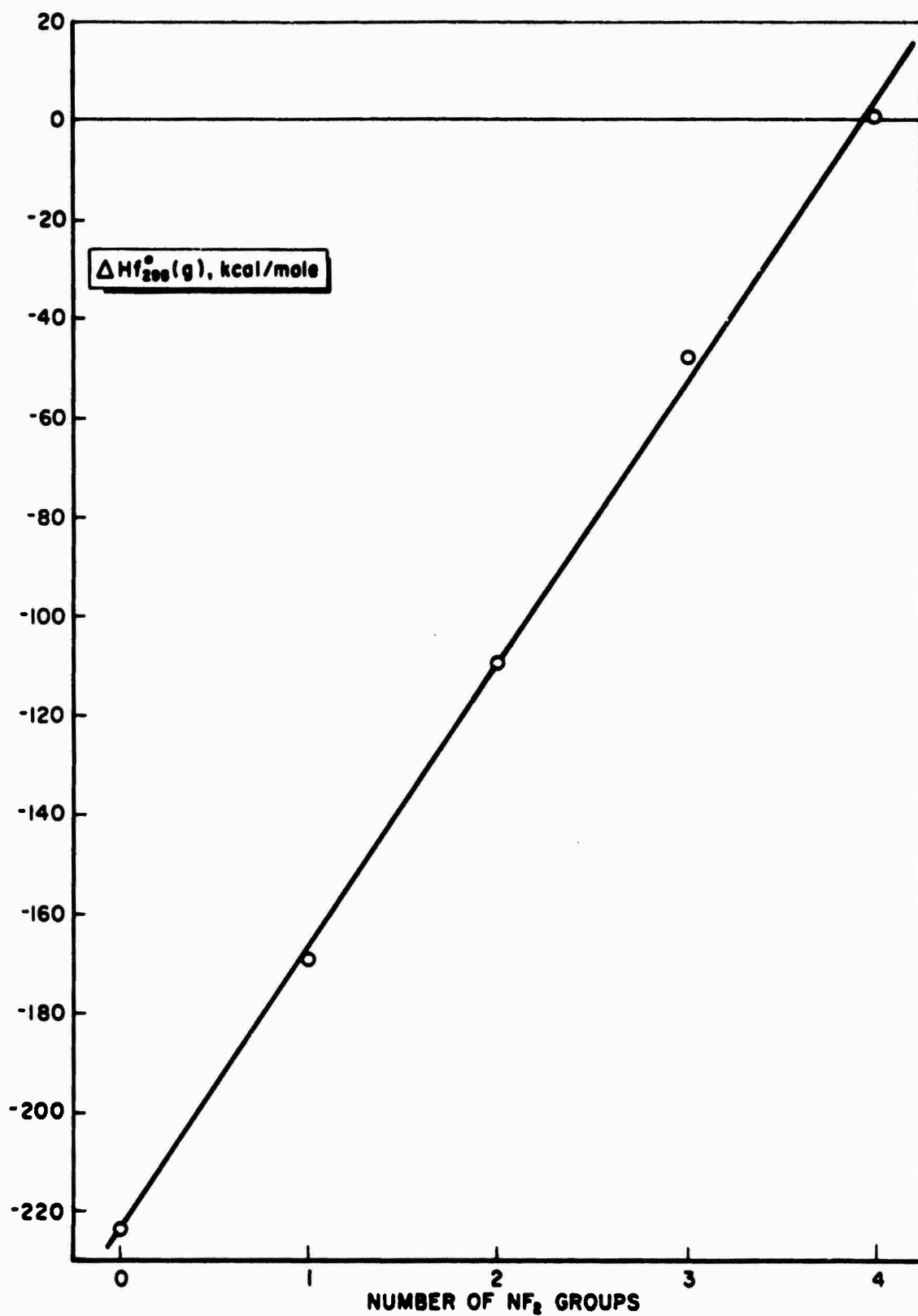
(U)   Fig. 5 - Heats of Formation of $CF_x(NF_2)_{4-x}$ Series

-38-

BEFORE MIXING **AFTER MIXING**
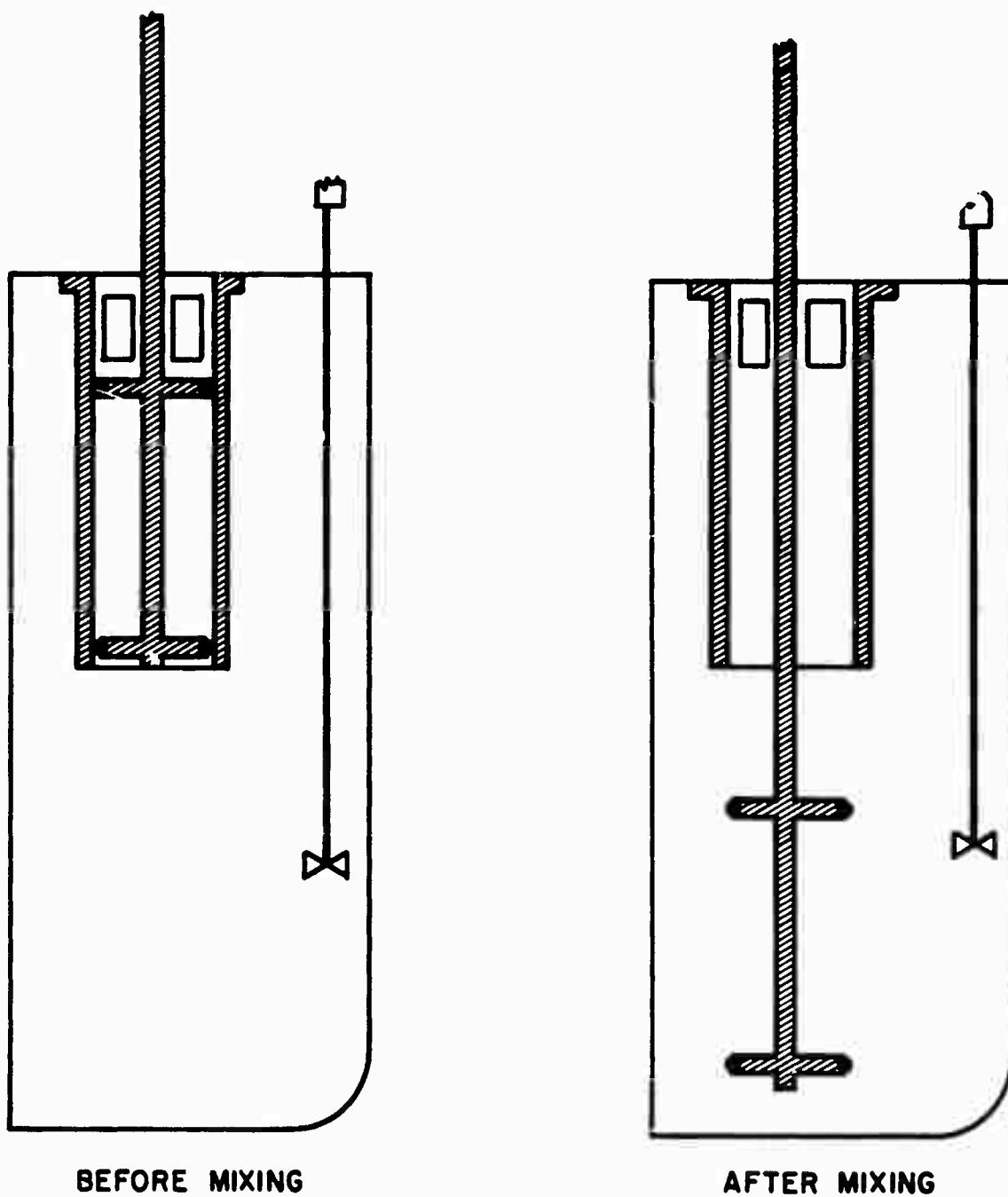
ALL SECTIONED PARTS ACRYLATE PLASTIC

(U) Fig. 6 - Combustion Calorimeter Adapted
for Heats of Mixing

-39-

3. Reagents (U)

(U) A nominal 1M solution of HCl was carefully titrated with base standardized against potassium acid phthalate and found to contain 0.000985 mole HCl per gram of solution. Chloride analysis of this solution agreed within 0.1%.

(U) Reagent grade $N_2H_6Cl_2$ was dissolved in water to form a nominal 1M solution. This solution was carefully analyzed for chloride and hydrazine and was found to contain 0.48204 mole $N_2H_6Cl_2$ and 0.01226 mole N_2H_5Cl per liter of solution.

(U) Reagent grade hydrazine was dissolved in water to form approximately a 1M solution. This solution was carefully analyzed and used as a stock solution for dilution to the desired state in each experiment. Analysis of this solution for ammonia revealed about 1 mole % ammonia relative to hydrazine.

(U) Chloride-free sodium hydroxide stock solutions were used for dilution to the appropriate state of each experiment.

4. Results (U)

(U) To check calorimeter performance, a series of runs on the heat of neutralization of HCl by NaOH was run. Fifty ml of HCl solution were placed in the chamber, while the bucket was filled with a solution containing about 20% excess NaOH. The use of excess NaOH avoids errors due to carbonate in the NaOH. Electrical calibration of the system gave E(calor) = 3589.8 cal/°C. Results of the neutralization runs are given in Table XXI.

Table XXI

Heat of Neutralization of HCl by NaOH at 24.7°C (U)

Exp. No.	Moles HCl	E(calor)xΔt	-ΔH(Neutralization), cal/mol
1	0.049912	689.21	13,808
2	0.049955	688.92	13,791
3	0.049915	688.49	13,793
4	0.049881	686.05	13,754
5	0.049925	687.95	13,780

Avg. 13,785 cal/mol

σ = 9 cal/mol

The average result given in Table XXI refers to the reaction:

$$HCl(54.7\ H_2O)\ +\ NaOH(3250\ H_2O) \rightarrow NaCl(3300\ H_2O)\ +\ H_2O$$
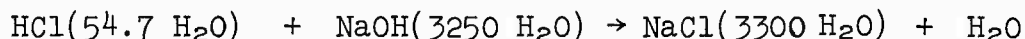
Hale, Izatt, and Christensen (18) and Vanderzee and Swanson (19) have published data on this reaction and are in excellent agreement with each other. For this reaction their data yield:

$$\Delta H(25°C)\ =\ -13,755\ cal/mol$$

With a ΔCp of reaction of -53.5 cal/mol/°C calculated from data given by Parker (20), we calculate:

$$\Delta H(24.7°C)\ =\ -13,772\ cal/mol$$

Our value is in excellent agreement and the calorimeter performance can be taken as satisfactory.

(U) The heat of mixing of 1M HCl and aqueous hydrazine was determined as a cross check on similar data by Howard and Skinner (17). Fifty ml of HCl solution were again placed in the chamber, while approximately 0.6 mole of N_2H_4 dissolved in 180 moles of water was charged to the bucket. Electrical calibration of the system gave $E(calor)$ = 3579.6 cal/°C. Results of five successful runs are given in Table XXII.

Table XXII

Heat of Mixing of HCl(aq) and Excess Hydrazine(aq)   (U)

Exp. No.	Moles HCl	E(calor)xΔt	$-\Delta H$(cal/mol)
2	0.049949	524.81	10,507
3	0.049902	525.63	10,533
4	0.049890	526.06	10,544
6	0.049883	524.88	10,522
7	0.049925	525.06	10,517

Avg. = 10,525 cal/mol

σ = 6 cal/mol

The average result from Table XXII refers to the reaction:

$$HCl(54.7\ H_2O)\ +\ 13(N_2H_4 \cdot 300\ H_2O) \rightarrow (N_2H_5Cl\ +\ 12\ N_2H_4\ +\ 3954.7\ H_2O)$$
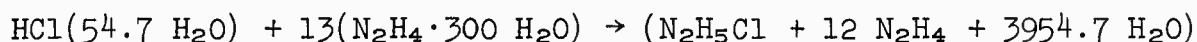
This duplicates almost exactly the system of Howard and Skinner (17) who, however, found $\Delta H = -10,450$ cal/mol. The difference is somewhat larger than the sum of the statistical errors and our higher value may be due to the 1% ammonia in our hydrazine, since ammonia has a slightly higher heat of neutralization. Inasmuch as Howard and Skinner did not analyze their hydrazine for ammonia, this must remain a matter of conjecture.

(U) The heat of mixing of aqueous hydrazine dihydrochloride and excess aqueous hydrazine was measured. Fifty ml of the analyzed $N_2H_6Cl_2$ solution were placed in the chamber and aqueous hydrazine in the bucket, so that, after mixing, the final solution was nearly identical with that in the HCl-N_2H_4 experiments. Electrical calibration of the system gave $E(calor) = 3626.2$ cal/°C. Results of four successful runs are given in Table XXIII.

Table XXIII

Heat of Mixing of $N_2H_6Cl_2$(aq) and N_2H_4(aq)   (U)

Exp. No.	Δt(°C)	Calories/Experiment
1	0.06788	246.15
2	0.06810	246.94
3	0.06810	246.94
4	0.06748	244.70
		Avg. = 246.18 cal/exp.

(U) The average result of Table XXIII refers to the process:

$$\begin{bmatrix} 0.024102 & N_2H_6Cl_2 \\ 0.000613 & N_2H_5Cl \\ 2.6734 & N_2O \end{bmatrix} + \begin{bmatrix} 0.60991 & N_2H_4 \\ 190.32 & H_2O \end{bmatrix} \rightarrow \begin{bmatrix} 0.048817 & N_2H_5Cl \\ 0.58581 & N_2H_4 \\ 193.00 & H_2O \end{bmatrix}$$
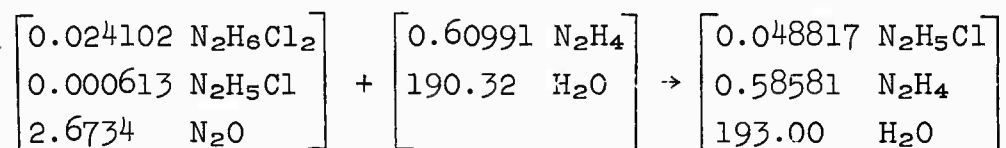
(U) Normalizing to one mole of HCl, adding algebraically to the previous result for $HCl + N_2H_4$, and neglecting dilution effects yield:

$$(HCl, 54.7 \ H_2O) + 0.50628(N_2H_4, 300 \ H_2O) \rightarrow \begin{bmatrix} 0.49372 & N_2H_6Cl_2 \\ 0.01256 & N_2H_5Cl \\ 54.7 & H_2O \end{bmatrix}$$

$$\Delta H = -5.482 \ \text{kcal}$$

-42-
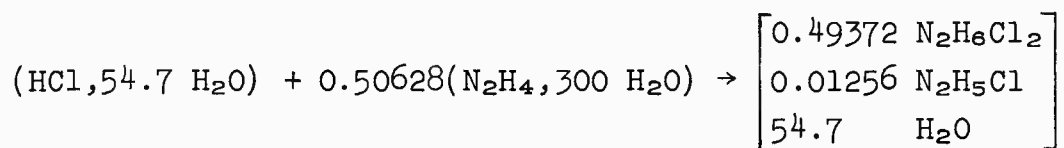
(U) Employing heats of formation of -39.533 kcal/mol for (HCl, 54.7 H$_2$O) (21) and +8.21 kcal/mol for (N$_2$H$_4$, 300 H$_2$O) (17), the heat of formation of the final mixture is calculated as -40.86 kcal. Employing -41.8 kcal/mol as the heat of formation of N$_2$H$_5$Cl(aq) (17) yields finally:

$$\Delta Hf_{298}(N_2H_6Cl_2, 110\ H_2O) = -81.7\ kcal/mol$$

This result is appreciably less negative than the -84.0 kcal/mol used in the early ClF$_5$ work. Revised calculations for ClF$_5$ are given in the next section.

5. Revised Heat of Formation of ClF$_5$ (U)

(U) Work cited in a previous report (14) was re-examined and recalculated by means of computer programs. The correction for oxidation of N$_2$H$_6$Cl$_2$ was also revised in accord with work described in the previous section. Revised calculations are given in Table XXIV.

Table XXIV

Revised Thermochemical Data for Hydrolysis of ClF$_5$ (U)

| Expt. No.	Mass ClF$_5$	E(calor)xΔt	N$_2$H$_6$Cl$_2$ corr.	ClO$_3$ corr.	-ΔHr cal/g
5	0.8708	-2094.9	1066.7	-15.7	1198.8
7	0.9783	-1640.8	456.6	- 1.1	1211.6
8	0.9738	-2377.1	1212.2	- 7.6	1204.0
11	1.0091	-2179.5	970.5	-11.3	1209.3

Avg. 1205.9 cal/g

(U) The average result of 1205.9 cal/g is appreciably lower than the original calculation of 1227.2 cal/g. With the new value and a molecular weight of 130.445:

$$\Delta Er = -157.30\ kcal/mol$$

correcting to constant pressure conditions:

$$\Delta Hr = -157.01\ kcal/mol$$

for the reaction at 25°C:

$$ClF_5(g) + 3 H_2O(\ell) \rightarrow (HCl, 22.8 H_2O) + 5(HF, 22.8 H_2O) + 3/2 O_2(g)$$
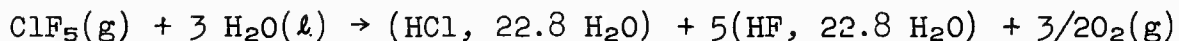
(U) The heat of formation depends on the selection of the heat of formation of HF(aq). If the latest selection of the National Bureau of Standards is employed (21), -76.29 kcal/mol, there is calculated:

$$\Delta Hf^\circ_{298}(ClF_5, g) = -58.8 \text{ kcal/mol.}$$

However, Lacher and Skinner (22) reviewed recent data and selected -77.01 for (HF, 22.8 H_2O), which gives:

$$\Delta Hf^\circ_{298}(ClF_5, g) = -62.4 \text{ kcal/mol}$$

6. Hydrazine Dihydrochloride in Combustion Calorimetry of Organic Chlorine Compounds (U)

(U) Smith, Scott, and McCullough (23) have thoroughly compared the use of hydrazine dihydrochloride and arsenious oxide as reductants in combustion calorimetry of organic compounds. They pointed out that for a test substance, 2,3,5,6-tetrachloroxylene, hydrazine dihydrochloride gave a lower heat of combustion than arsenious oxide. They noted that the heat of formation of $N_2H_6Cl_2$ was not well established and their experiments favored a more negative value. Unfortunately, the present work indicates a less negative value for the heat of formation of aqueous $N_2H_6Cl_2$ than that used by Scott et al. The discrepancy is therefore increased, and the reason for the discrepancy must be found elsewhere than in the heat of formation of the reductant.

G. HEAT OF COMBUSTION OF ANILINE HYDROCHLORIDE (U)

1. Introduction (U)

(U) Perchlorates are important compounds in propellant chemistry. Thermochemical data have been obtained on such compounds as nitronium perchlorate, hydrazine diperchlorate, and INFO-635 by various means. Many inorganic perchlorates and all organic perchlorates can be thermochemically investigated by the heat of combustion technique. Baroody and coworkers (24) have published an outline for the calculation of heats of formation of compounds containing C, H, Cl, N, and O from raw heat of combustion data. The heat of combustion of aniline hydrochloride was determined to test this outline as well as our laboratory techniques. The heat of formation of aniline hydrochloride can be determined by a heat of solution approach as a check on the combustion result.

2. Material (U)

(U) Aniline hydrochloride was prepared by dissolving about 29 g in 365 ml of dry ether and bubbling in dry hydrogen chloride

until it was no longer absorbed. About 34 g (85% of theory) of
white product was separated by filtration and washed with 300 cc
of dry ether. The product was dried by heating overnight in a
vacuum oven at 50°C. The dried material melted sharply at 198°C
(literature m.p. 198°C) and analyzed 27.3% chlorine (theory 27.3%).
The purity by reaction with bromine was 99.8%.

(U) A sample of Dow aniline with a purity of 99.9 mole % by
freezing curve analysis was used for heat of solution work.

3. Equipment (U)

(U) A typical rotating bomb calorimeter and a platinum-lined
combustion bomb were employed for the heat of combustion studies.
For heat of solution work the same type of equipment was used,
except that a glass ampoule attached to a breaking mechanism was
substituted for the bomb in the calorimeter.

4. Procedure (U)

(U) Samples were pelleted and placed in a platinum crucible
which was then suspended in a gimbal attached to the bomb lid.
Approximately 20 g of 0.08 M As_2O_3 solution was accurately metered
to the bomb by means of a weight buret. The bomb was closed and
charged with purified oxygen to 30 atm pressure. After equilibrium
in the calorimeter, the charge was electrically fired and the re-
sulting heat release measured by means of an automatic resistance
bridge. After the calorimetry the bomb was carefully discharged,
opened, and the solution recovered for analysis for nitrate and
unoxidized arsenious oxide.

(U) For heat of solution studies, aniline hydrochloride or
liquid aniline was sealed in a thin walled glass ampoule and the
calorimeter canister was filled with water containing a slight
excess of NaOH (for aniline hydrochloride) or a corresponding mix-
ture of NaCl and NaOH (for aniline). At the appropriate moment,
the ampoule was broken and the solution process took place.

5. Calculations (U)

(U) The outline published by Baroody et al. (24) was programmed
for computer calculation. Some of the necessary parameters were
estimated, while others were taken from recent publications. A
list of these parameters is given in Table XXV. Constant factors
for the computer program are given in Table XXVI.

6. Results (U)

(U) The heat of combustion results are tabulated in Table XXVII.
The average value and a molecular weight of 129.5904 yield:

$$\Delta E_c^\circ = -799.52 \pm 0.29 \text{ kcal/mole}$$

-45-

corresponding to the reaction:

$$C_6H_8ClN(c) + 3 \tfrac{1}{4} O_2(g) \rightarrow 6 CO_2(g) + \tfrac{1}{2} N_2(g) + HCl(600 H_2O)$$

$$+ \tfrac{7}{2} H_2O(\ell)$$
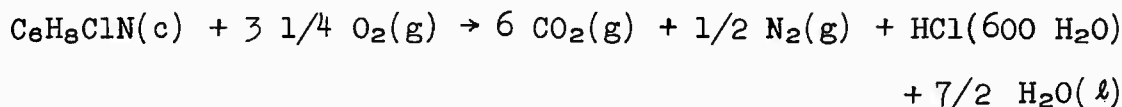
Correcting to constant pressure conditions:

$$\Delta H_c^\circ = -800.26 \pm 0.29 \text{ kcal/mole.}$$

With auxiliary data from Wagman et al. (21),

$$\Delta H f^\circ_{298} = -42.97 \pm 0.29 \text{ kcal/mole}$$

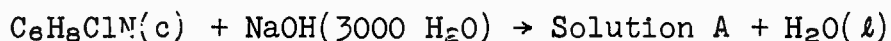(The uncertainty is taken as twice the standard deviation.)

Table XXV

Parameters for Washburn Corrections
for C-H-Cl-N-O Compounds

Item	Symbol	Value	Reference
29h	g^i	0.9973	Estimated
51	$K(CO_2)$	0.033	(25)
66	g^f	[0.996 - 0.0137 at % (HCl)]	Estimated
69	$\left[\dfrac{\partial E}{\partial P}\right]_T^i$ (soln)	-0.00186 cal/g atom	Estimated
69a	$\left[\dfrac{\partial E}{\partial P}\right]_T^f$ (soln)	-0.00170 cal/g atom	Estimated
71b	$\Delta E(CO_2)$soln	-4000 cal/mole	Estimated cf. (25)
91a	$\Delta E(As_2O_5)$decomp	76500 cal/mole	(26)

(U) Results of the heat of solution work are given in Table XXVIII. Electrical calibration of the system gave E(calor) as 3667 ± 3 cal/°C. From the data there is derived:

(1) $\Delta H = 3.37$ kcal/mole for the reaction:

$$C_6H_8ClN(c) + NaOH(3000 H_2O) \rightarrow \text{Solution A} + H_2O(\ell)$$

-46-

(ii) $\Delta H = -0.58$ kcal/mole for the reaction:

Solution A $\rightarrow$ $C_6H_7N(\ell)$ + NaCl(3000 H_2O)
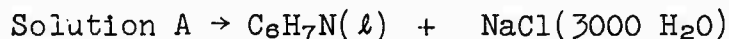
(iii) $\Delta H = -3.95$ kcal/mole for the reaction:

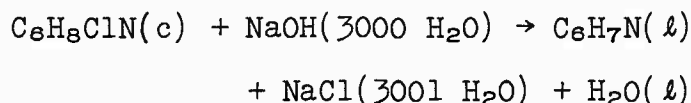$C_6H_8ClN(c)$ + NaOH(3000 H_2O) $\rightarrow$ $C_6H_7N(\ell)$

+ NaCl(3001 H_2O) + $H_2O(\ell)$

With auxiliary data for NaOH, NaCl, and H_2O from Wagman et al. (21) and the heat of formation of liquid aniline, +7.47 ± 0.20 kcal/mole, from Hatton et al. (27), there is derived for aniline hydrochloride:

$$\Delta Hf_{298}^\circ = -42.0 \pm 0.3 \text{ kcal/mole}$$

Table XXVI

Constant Factors for Calculations of Heat of Combustion of Aniline Hydrochloride

Formula of compound	C_6H_8ClN
Formula of fuse	$CH_{1.8}O_{0.9}$
Density of compound	1.222
Density of fuse	1.5
Bomb volume	0.349 liter
Initial oxygen pressure at 25°C	30.3 atm
Reference temperature	25°C
Final ratio H_2O/HCl	600
$(\partial E/\partial P)_T$ of compound	-0.003 cal/g/atm
ΔE_c° of fuse	-111.7 kcal/mole
Cp of compound	0.29 cal/g/°C
Cp of fuse	0.4 kcal/g/°C
E(calor)	3427.20 cal/°C

(U)   The difference between the combustion and solution results is slightly larger than the combined statistical errors, pointing to a small systematic error in one or both approaches. The difference is not serious, however, and it appears that the heat of formation of C-H-Cl-N-O compounds, such as organic perchlorates, can be determined with satisfactory accuracy by the heat of combustion method.

Table XXVII

Heat of Combustion of Aniline Hydrochloride (U)

Parameter	Experiment Number					
	1	2	3	4	5	6
Sample wt. g	1.08917	1.08383	1.09075	1.09204	1.09822	1.10036
Fuse, g	0.00415	0.00375	0.00278	0.00341	0.00310	0.00312
$N^1(H_2O)$	1.1558	1.1553	1.1668	1.1561	1.1548	1.1558
$N^1(As_2O_3)$	0.002104	0.002108	0.002126	0.002134	0.002133	0.002124
$N^f(HNO_3)$	0.000564	0.000661	0.000645	0.00613	0.000693	0.000774
$N^f(H_2PtCl_6)$	0.00017	0.000011	0.000012	0.000018	0.000009	0.000010
$N^f(As_2O_3)$	0.001344	0.001334	0.001323	0.001339	0.001352	0.001285
ΔE_{ign}, cal	0.47	0.41	0.40	0.39	0.41	0.38
t_1, °C	22.96672	22.96672	22.96678	22.96671	22.96668	22.96675
t_f, °C	25.01183	25.00306	25.01360	25.02069	25.03117	25.03836
Δt_{corr}, °C	0.06976	0.06963	0.06913	0.07452	0.07368	0.07431
$-\Delta Ec/M$ (cal/g)	6169.63	6172.03	6169.66	6166.04	6168.38	6171.64

Average $-\Delta Ec/M$ = 6169.56 cal/g

Std. Dev. = 1.11 cal/g

Table XXVIII

Heat of Solution of Aniline and
Aniline Hydrochloride in Aqueous NaOH

Expt. No.	Sample Mass, grams	Corrected Temp. Rise, °C	Heat of Solution, cal/g
1[a]	6.9311	0.04910	-25.98
2[a]	6.9227	0.04919	-26.06
3[b]	5.007	-0.00614	+ 4.50

[a]Aniline hydrochloride.
[b]Aniline

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13 ABSTRACT

Heats of formation of several compounds of interest in the area of rocket propellants were measured by combustion and/or reaction calorimetry. Results in kcal/mole were: Perfluoroammonium fluorborate (NF_4BF_4), -337.4; methyldiazabicyclooctane ($C_7H_{14}N_2$), +2.99; a compound of code name DOA and formula $C_2H_{12}O_4N_4$, -48.24; perfluoromethylamine (CF_5N), -168.9; chlorine pentafluoride (ClF_5), 62.4; binder ingredient PEAA, -8.28 kcal/100 g; binder ingredient PBAN, -0.70 kcal/100 g; and aniline hydrochloride (C_8H_8ClN), -42.97.

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Heat of Formation Perfluoroammonium Fluoborate Aminoethylaziridine Methyldiazabicyclooctane Code Name DOA Perfluoromethylamine Chlorine Pentafluoride Binder Ingredient PBAA Binder Ingredient PBAN Aniline Hydrochloride							

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